A summation procedure that improves the accuracy of the fourth-order Mo/ller–Plesset perturbation theory

David Z. Goodson

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

COMMUNICATIONS

A summation procedure that improves the accuracy of the fourth-order Møller–Plesset perturbation theory

David Z. Goodson
Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

A procedure is demonstrated for summing the Møller–Plesset many-body perturbation expansion based on the ability of quadratic summation approximants to locate branch point singularities in the complex plane of the perturbation parameter. Accuracy comparable to that from CCSDT coupled-cluster calculations is obtained using fourth-order perturbation theory. © *2000 American Institute of Physics.* [S0021-9606(00)31240-5]

Fourth-order Møller–Plesset perturbation theory (MP4) is a widely used method for including electron correlation in quantum chemical calculations. It belongs to the MPn hierarchy, in which MP1 is the Hartree–Fock approximation. Each increase in n significantly increases the computational cost and, in principle, the accuracy. However, serious concerns have been expressed about uneven convergence, and in some cases divergence, of the MPn sequence.[1–7]

The MPn sequence for the energy, E, can be expressed as an asymptotic expansion

$$E(z) \sim \sum_{i=1}^{n} E_i z^{i-1} \tag{1}$$

in terms of a variable z, such that $E(0) = E_1$ is the Hartree–Fock energy while $E(1) = E_1 + E_2 + \cdots + E_n$ is the MPn result. The convergence of this sequence is strongly affected by the presence of branch points of the function $E(z)$ in the complex z plane.[8,9] These are nonphysical values of z at which the energy eigenvalues of two different states with the same symmetry become equal. Since Eq. (1) expresses $E(z)$ as a polynomial, which is single valued at all z, there is a limit to the accuracy with which that expression can describe the true $E(z)$, which is double valued at the branch points.

Here a summation procedure is proposed for mitigating the effects of branch points on the MPn sequence. The *partial summation approximant* given by Eq. (1) is replaced with a *quadratic approximant*,[10,11] which explicitly includes square-root branch points. The locations in the z plane at which these approximants place the branch points are determined, and then the perturbation theory is repartitioned so as to shift the nearest branch point away from the origin.

Quadratic approximants, $S_{[L/M,N]}$, are constructed from three polynomials, $P_L(z)$, $Q_M(z)$, and $R_N(z)$, of degrees L, M, and N, respectively, according to

$$S_{[L/M,N]} = \frac{1}{2} \left[\frac{P_L}{Q_M} \pm \frac{1}{Q_M} \sqrt{P_L^2 - 4Q_M R_N} \right]. \tag{2}$$

The coefficients of the three polynomials are determined by the condition that the coefficients of the Taylor expansion of

$S_{[L/M,N]}$ in powers of z be equal to the corresponding coefficients E_i of the energy expansion. The function $S_{[L/M,N]}(z)$ has two branches connected by branch points at the roots of the discriminant polynomial $P_L^2 - 4Q_M R_N$.

The large-order behavior of the energy expansion is determined by the *dominant* branch point z_d, which is the branch point of $E(z)$ nearest the origin. It is useful to classify systems according to whether z_d is in the positive half-plane (class A) or the negative half-plane (class B).[9,11–13] For class A systems the branch point is expected to connect the eigenstate under consideration with the next higher eigenstate of the same symmetry in the physical ($z=1$) spectrum. For class B systems z_d is expected to lie on the negative real axis. It connects the eigenstate under consideration with a nonphysical autoionizing state.[3,9,14] Qualitative criteria have been formulated for determining the class of a given system based on the nature of the electron orbital structure.[13] Class B contains systems with clustering of electrons pairs, such as electron-rich atoms or molecules with multiple bonds. Class A contains systems with well-separated electron pairs. In principle the class B singularity is best described by constraining the polynomial R_N with the condition $R_N(0)=0$ while for class A it is best to leave $R_N(0)$ unconstrained.[11]

z_d can be shifted away from the origin by repartitioning the perturbation theory. This involves redefining the "perturbation" in such a way that the solution for the energy remains the same at $z=1$ but is changed elsewhere in the z plane. A particularly convenient repartitioning is the Feenberg transformation,[15] which amounts to a simple rearrangement of Eq. (1) in terms of an arbitrary parameter λ, with the E_i replaced by[12]

$$E_i^{(\lambda)} = \sum_{k=1}^{i-1} \binom{i-2}{k-1} \lambda^{i-k-1}(1-\lambda)^k E_{k+1} \tag{3}$$

for $i \geq 2$, with $E_1^{(\lambda)} = E_1$. The effect on the singularity structure is shown in Fig. 1 for the BH molecule. The upper panel shows the locations of the two branch points of the $S_{[1/0,1]}$ approximant while the lower panel shows the error in the result for the energy. This behavior of z_d as a function of λ
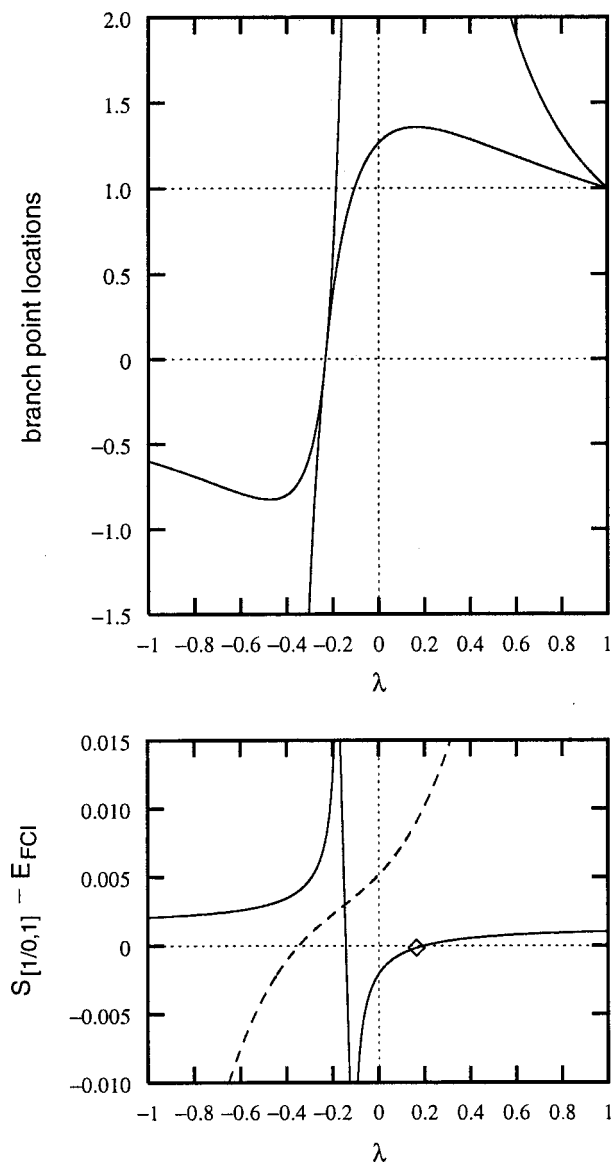
FIG. 1. Branch point locations and error (in units of E_h) of the $[1/0,1]$ approximant for the ground state energy of BH, as a function of the repartitioning parameter λ. The dashed curve shows the error from MP4 partial summation. The diamond marks the error corresponding to the value of λ that maximizes the distance from the origin of the dominant branch point. The perturbation series is from Leininger *et al.* (Ref. 7) with the aug-cc-pVQZ basis set.

for MP4 is typical. For λ sufficiently negative, z_d is found on the negative real axis with a maximum in $|z_d|$ typically around $\lambda = -0.4$ for class A and $\lambda = -0.2$ for class B. As λ becomes more positive, z_d eventually shifts to the positive half-plane with a maximum in $|z_d|$ in the approximate range $-0.1 < \lambda < 0.5$ that is always the global maximum.

Table I shows results for various class A systems for which full configuration-interaction (FCI) results are available for comparison. For class A the $[1/0,1]$ unconstrained quadratic approximant with λ corresponding to the maximum in the positive half-plane (''qu$\lambda+$'') dependably gives higher accuracy than partial summation and is usually at least as accurate, and often much more accurate, than the unshifted ($\lambda=0$) quadratic approximant. Also shown in Table I are coupled-cluster results using the same basis sets. The computational cost of MP4 scales as N^7 with the size N of the basis. This is roughly comparable to the cost of the CCSD(T) method (coupled-cluster with singles and doubles and perturbative treatment of triples[21–23]), while CCSD scales as N^6 and CCSDT as N^8. Although the MP4 partial sums are comparable in accuracy to the less expensive CCSD, the singularity-shifted quadratic sums are on average slightly more accurate than CCSDT, which is considerably more expensive. The one system in the table for which the CCSD(T) and CCSDT results are superior is the $^1A_1$ state of CH_2, which has a relatively small gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the same symmetry.[9,24]

Results for class B systems are shown in Tables II and III, from the $[1/0,2]$ constrained approximant. Also shown is the $[1/1,1]$ approximant, the value of which is independent of λ at the point $z=1$. This approximant was studied in Ref. 11. It is often extremely accurate but on average is less dependable than the singularity-shifted $[1/0,2]$ approximants. These tables also show z_d for the $[1/0,2]$ approximant at the λ that shifts z_d as far as possible into the negative half-plane (''qc$\lambda-$''). For class B there is an approximate correlation between the accuracy of the quadratic approximant and how far away from the origin the repartitioning is able to shift the singularity, with a very significant decrease in accuracy if z_d cannot be shifted past -1. The results have been grouped as ''well-behaved'' or ''difficult'' according to whether or not

TABLE I. Class A systems: $\Delta E = E_{approx} - E_{FCI}$ in mE_h.

Method	BH[a]	NH$_2$ $^2B_1$[b]	NH$_2$ $^2A_1$[b]	CH$_2$ $^3B_1$[b]	CH$_2$ $^1A_1$[b]	CH$_3$[b]	Mean $|\Delta E|$	Median $|\Delta E|$
MP4 qu $\lambda+$[c]	−0.155	−0.055	0.008	0.270	1.926	0.126	0.423	0.141
MP4 qu[c]	−2.060	−0.480	−0.332	0.297	1.925	0.129	0.871	0.406
MP4 sum	5.162	1.900	1.617	1.880	4.979	1.981	2.920	1.941
CCSD	2.740	3.211	2.992	2.090	3.544	2.790	2.895	2.891
CCSD(T)	0.501	0.547	0.532	0.360	0.873	0.499	0.552	0.517
CCSDT	0.090	−1.274	0.223	0.017	0.207	−0.744	0.426	0.215

[a]E_i and CC values from Ref. 7 with aug-cc-pVQZ basis, $E_{FCI} = -25.235\,843\,E_h$.
[b]E_i from Ref. 16 with the DZP basis; CC values, Ref. 17; $E_{FCI} = -55.742\,620$(NH$_2$ $^2B_1$), $-55.688\,762$ (NH$_2$ $^2A_1$), Ref. 18, $-39.046\,260$ (CH$_2$ $^3B_1$), $-39.027\,183$ (CH$_2$ $^1A_1$), Ref. 19, and $-39.721\,212$ (CH$_3$), Ref. 20, in E_h.
[c]qu$\lambda+$ and qu are $[1/0,1]$ unconstrained approximants, the former with the λ that maximizes $|z_d|$ in the positive half plane, the latter with $\lambda=0$.

J. Chem. Phys., Vol. 113, No. 16, 22 October 2000

Summation of perturbation series   6463

TABLE II. Well-behaved class B systems[a]: $\Delta E = E_{approx} - E_{FCI}$ in mE_h. The last row lists the position of the dominant singularity in the MP4 qc $\lambda -$ approximant.

	Ar[b]	Cl[−b]	HCl[b]	F[c]	Ne[d]	H$_2$O[e]	F[−f]	HF[b]	Mean $|\Delta E|$	Median $|\Delta E|$
MP4 qc $\lambda +$[g]	0.226	0.120	0.152	0.029	−0.947	0.675	−0.235	−0.599	0.373	0.231
MP4 qc $\lambda -$[g]	0.229	0.140	0.174	0.102	−0.857	0.784	−0.086	−0.447	0.352	0.202
MP4 [1/1,1][g]	0.216	−0.013	−0.007	−0.319	−1.447	0.200	−1.140	−1.684	0.628	0.268
MP4 sum	0.490	0.752	1.131	0.529	−0.981	1.060	−1.016	−0.882	0.855	0.932
CCSD	2.968	4.805	4.718	3.432	2.972	3.744	5.109	4.707	4.432	4.231
CCSD(T)	0.443	0.689	0.695	0.219	0.181	0.658	0.208	0.536	0.454	0.490
CCSDT	0.253	0.370	0.340	−0.015	0.061	0.493	0.232	0.335	0.262	0.294
z_d	−6.50	−3.32	−3.19	−2.49	−2.33	−2.32	−2.04	−1.90		

[a]A "well-behaved" class B system is defined as one for which $z_d < -1.5$ after singularity shifting.
[b]E_i, CC, and FCI values from Ref. 7 with aug-cc-pVQZ basis, $E_{FCI} = -526.970\ 128$ (Ar), $-459.738\ 991$ (Cl$^-$), $-460.272\ 768$ (HCl), $-100.264\ 177$ (HF), in E_h.
[c]E_i from Ref. 16 with the $[5s4p2d]$ basis, CC values from Refs. 25 and 26, $E_{FCI} = -99.594\ 877\ E_h$ from Ref. 19.
[d]E_i and FCI values from Ref. 2 with aug-cc-pVDZ basis, CC values from Ref. 28, $E_{FCI} = -128.709\ 476\ E_h$.
[e]E_i, CC, and FCI values from Ref. 29 with the cc-pVDZ basis, $E_{FCI} = -76.241\ 860\ E_h$.
[f]E_i and FCI values from Ref. 2 with the cc-pVTZ-(f) basis, CC values from Ref. 28, $E_{FCI} = -99.675\ 158\ E_h$.
[g]qc $\lambda +$ and qc $\lambda -$ are the [1/0,2] approximants with the constraint $R_2(0) = 0$ and z_d in the positive or negative half-plane, respectively. [1/1,1] is the λ-independent diagonal approximant with the constraint $R_1(0) = 0$.

z_d for the qc $\lambda -$ approximant is shifted beyond -1.5.

The source of the difficulty appears to be the need to simultaneously model the nonphysical branch point on the negative real axis and a nondominant branch point in the positive half-plane. A good example of this is F$^-$, for which the tables contain results from three different basis sets. The worst qc $\lambda -$ result comes from the aug-cc-pVDZ basis,[31] which contains diffuse functions that easily describe autoionizing states. In this case the quadratic approximants do relatively poorly at MP4 but are extremely accurate at MP6, which is the first order at which the approximants clearly discern both kinds of singularities. At MP6 the maximum $|z_d|$ corresponds to $\lambda = 0.37$, with equidistant branch points at ± 1.8. For F$^-$ with the cc-pVTZ-(f) basis,[2] which is the same size as the aug-cc-pVDZ basis but omits the diffuse functions, z_d is farther from the origin and the accuracy of the MP4 approximants is much higher. The MP4 quadratic approximants, for all systems studied here, place all singularities either in the positive half-plane or in the negative half-plane, with a rapid transition at an intermediate value of λ. Apparently, as long as the dominant singularity is far enough from the origin it is sufficient to model the singularity structure in only one of the two regions.

The systems in Table III are difficult for MP4, but can also be difficult for the coupled-cluster methods. For such systems (and for class A systems with physical near degeneracies) it is perhaps best to use a multireference state theory[24,32–34] summed with quadratic approximants, or a more powerful repartitioning technique,[8] rather than to try to resum the conventional MP4 expansion coefficients provided by standard software packages. However, for the well-behaved class B systems the results at MP4 from the qc $\lambda \pm$ approximants are somewhat better than the CCSD(T) results and comparable in accuracy to the CCSDT results. Good results are obtained at either of the two maxima.

TABLE III. Difficult class B systems[a]: $E_{approx} - E_{FCI}$ in mE_h. The last row lists the position of the dominant singularity in the MP4 qc $\lambda -$ approximant.

	F[−b]	F[−c]	N$_2$[d]	C$_2$[d]	CN$^+$[d]
MP4 qc $\lambda +$	−1.784	−2.447	1.193	19.385	25.805
MP4 qc $\lambda -$	−1.482	−2.165	1.643	20.203	26.687
MP4 sum	−5.398	−5.502	−2.221	−8.062	−21.933
CCSD	7.715	6.679	14.442	29.957	33.193
CCSD(T)	0.285	0.735	1.862	2.042	−0.231
CCSDT	0.273	0.397	1.834	3.371	3.290
z_d	−1.42	−1.36	−1.28	−0.73	−0.68

[a]A "difficult" class B system is defined as one for which $z_d > -1.5$ after singularity shifting.
[b]E_i from Ref. 16 with the $[5s4p2d]$ basis, CC values from Refs. 25 and 30, $E_{FCI} = -99.706\ 690$ from Ref. 27.
[c]E_i and FCI value from Ref. 2 with the aug-cc-pVDZ basis, CC values from Ref. 28, $E_{FCI} = -99.669\ 369\ E_h$.
[d]E_i, CC, and FCI values from Ref. 7 with the cc-pVDZ basis, $E_{FCI} = -109.278\ 340$ (N$_2$), $-75.729\ 853$ (C$_2$), $-91.997\ 969\ E_h$ (CN$^+$).

[1]P. M. W. Gill and L. Radom, Chem. Phys. Lett. **132**, 16 (1986).
[2]J. Olsen, O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **105**, 5082 (1996).
[3]O. Christiansen, J. Olsen, P. Jørgensen, H. Koch, and P.-Å. Malmqvist, Chem. Phys. Lett. **261**, 369 (1996).
[4]T. Helgaker, J. Gauss, P. Jørgensen, and J. Olsen, J. Chem. Phys. **106**, 6430 (1997).
[5]T. H. Dunning, Jr. and K. A. Peterson, J. Chem. Phys. **108**, 4761 (1998).
[6]H. Larsen, A. Halkier, J. Olsen, and P. Jørgensen, J. Chem. Phys. **112**, 1107 (2000).
[7]M. L. Leininger, W. D. Allen, H. F. Schaefer III, and C. D. Sherrill, J. Chem. Phys. **112**, 9213 (2000).
[8]K. Dietz, Ch. Schmidt, M. Warken, and B. A. Heß, J. Phys. B **26**, 1885 (1993).
[9]J. Olsen, P. Jørgensen, T. Helgaker, and O. Christiansen, J. Chem. Phys. **112**, 9736 (2000).
[10]R. E. Shafer, SIAM (Soc. Ind. Appl. Math.) J. Math. Anal. **11**, 447 (1975).
[11]D. Z. Goodson, J. Chem. Phys. **112**, 4901 (2000).
[12]Ch. Schmidt, M. Warken, and N. C. Handy, Chem. Phys. Lett. **211**, 272 (1993).
[13]D. Cremer and Z. He, J. Phys. Chem. **100**, 6173 (1996).

[14] F. H. Stillinger, J. Chem. Phys. **112**, 9711 (2000).

[15] E. Feenberg, Phys. Rev. **103**, 1116 (1956).

[16] Z. He and D. Cremer, Int. J. Quantum Chem. **59**, 71 (1996).

[17] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).

[18] C. W. Bauschlicher, Jr., S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, J. Chem. Phys. **85**, 1469 (1986).

[19] C. W. Bauschlicher, Jr. and P. R. Taylor, J. Chem. Phys. **85**, 6510 (1986).

[20] C. W. Bauschlicher, Jr. and P. R. Taylor, J. Chem. Phys. **86**, 5600 (1987).

[21] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[22] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).

[23] J. F. Stanton, Chem. Phys. Lett. **281**, 130 (1997).

[24] R. K. Chaudhuri and K. F. Freed, J. Chem. Phys. **107**, 6699 (1997).

[25] G. E. Scuseria, J. Chem. Phys. **95**, 7426 (1991).

[26] J. D. Watts and R. J. Bartlett, J. Chem. Phys. **93**, 6104 (1990).

[27] C. W. Bauschlicher, Jr. and P. R. Taylor, J. Chem. Phys. **85**, 2779 (1986).

[28] M. L. Leininger (private communication).

[29] J. Olsen, P. Jórgensen, H. Koch, A. Balkova, and R. J. Bartlett, J. Chem. Phys. **104**, 8007 (1996).

[30] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987); **89**, 3401 (1988).

[31] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[32] G. Hose, J. Chem. Phys. **84**, 4505 (1986).

[33] K. Hirao, Int. J. Quantum Chem., Quantum Chem. Symp. **26**, 517 (1992).

[34] S. R. Gwaltney and M. Head-Gordon, Chem. Phys. Lett. **323**, 21 (2000).