Singularity analysis of fourth-order Møller–Plesset perturbation theory

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Abstract

The usefulness of Møller–Plesset perturbation theory, a standard technique of quantum chemistry, is determined by singularities in the corresponding energy function in the complex plane of the perturbation parameter. A method is developed that locates singularities from fourth-order perturbation series, using quadratic approximants with bilinear conformal mappings.
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Many-body perturbation theory is one of the earliest techniques for solving the Schrödinger equation. In the version developed by Møller and Plesset [1] the Hartree–Fock approximation is used for the zeroth-order wavefunction and Rayleigh–Schrödinger perturbation theory is used to determine higher-order corrections. The fourth-order theory (MP4) was formerly considered a method of choice for high-accuracy ab initio quantum chemistry on account of an apparently favorable balance of accuracy and computational cost. However, concerns have been raised concerning the perturbation series convergence [2–8]. As a result, this method has largely been replaced in practice by the CCSD(T) coupled cluster theory [9].

The underlying causes of poor convergence have recently been elucidated in terms of the singularity structure of the energy function [10–15], and a summation method for MP4 has been proposed that improves the summation accuracy by modeling the singularity structure [16,17]. The success of the summation can depend on having advance knowledge of singularity locations. However, the singularity analyses were carried out using full configuration-interaction (FCI) calculations and per-

turbation series of very high order, which have a much higher computational cost than MP4. The problem we address here is how to characterize the singularity structure given only the fourth-order asymptotic series.

The perturbation theory can be formulated from a partitioning of the Hamiltonian [18],

$$H(z) = H_0 + z(H_{phys} - H_0), \qquad (1)$$

in terms of a perturbation parameter z. H_{phys} is the true Schrödinger Hamiltonian while H_0 is the sum of one-particle Fock operators. The ground-state energy eigenvalue is obtained as a power series in z with the physical solution corresponding to $z = 1$. This power series is the asymptotic series of a function $E(z)$, and the accuracy with which the series can be summed depends on the locations of singular points in the complex z plane. Functional analysis predicts there will be two classes of singularities [11,13,14,19,20]. Class α singularities are complex-conjugate pairs of isolated square-root branch points [19]. They represent avoided crossings of the ground-state energy and the energy of the first excited state of the same symmetry for a path along the real z axis. Class β singularities are critical points that lie on the real axis [11,14,20].

The critical points, in principle, are branch points with a complicated functional form [20,21]. This would be true, at least, if the *exact* Hartree–Fock wavefunction were used as

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the zeroth-order solution. In practice, an approximation to the Hartree–Fock solution is used, with the wavefunction as a linear combination in a finite-dimension basis set. In that case, the function $E(z)$ is approximated as an eigenvalue of a finite real matrix. This is the full configuration-interaction energy, $E_{\text{FCI}}(z)$, which can only have square-root branch points, in complex-conjugate pairs [19,21]. Thus, the class α singularities are accurately modeled but the class β singularities are not. In practice, $E_{\text{FCI}}(z)$ models a class β critical point of $E(z)$ with a cluster of square-root branch point pairs with small imaginary parts [14].

In previous work we studied singularities of $E_{\text{FCI}}(z)$ using two approaches. First, we computed the FCI energy spectrum at many different values of real z and determined the branch point locations from analysis of avoided crossings with the ground state [14]. Because each FCI computation is very costly, this strategy is inefficient, and the analysis was carried out for only a few systems. Subsequently, we determined singularity structure for a larger set of systems by analyzing the high-order behavior of the asymptotic series [15]. The series coefficients can be determined to high order with high precision using intermediate quantities obtained in the course of an FCI computation [4, 8,22–25]. Thus, a single FCI computation is sufficient to determine the locations of the several branch points closest to the origin in the z plane.

Because of the high computational cost, any method requiring an FCI computation is practical at present only for systems with no more than approximately 10 correlated electrons. For routine applications one is limited to MP4, which can be efficiently computed from explicit formulas [18]. Fourth order is too low for standard methods of singularity analysis to be of much use. Asymptotic methods such as the D'Alembert ratio test and its more sophisticated variants [26–28] have rigorous convergence theorems, but for low-order MP series nonsingular contributions are so large that the theorems are irrelevant. Furthermore, because these methods have as their foundation Darboux's theorem concerning the infinite-order limit of the series coefficients as determined by the dominant singularity [26,29], they are poorly suited to studying nondominant singularities. The typical singularity structure of $E_{\text{FCI}}(z)$ is to have singularities in both the negative and positive half planes approximately equidistant from the origin, and, as a result, the convergence of the series at fourth order often cannot be accounted for by just the dominant singularity structure [15].

A more promising strategy is to use an *approximant*, an arbitrary function containing parameters that are fit to the asymptotic series of the true function. The advantage is that if the functional form of the approximant is a good match for that of the true function, an accurate model can be obtained with very few parameters. We know that the singularities of $E_{\text{FCI}}(z)$ are square-root branch points and we can design the approximant accordingly. A straightforward approach for modeling square-root branch points is a quadratic approximant [30,31]. However, for MP4 with complex-conjugate branch-point pairs in both half planes at approximately the same distance from the origin, these approximants attempt to simultaneously model all the singularities with one or two branch points approximately

midway between the true ones [10], which is a very poor model of the true functional form. We demonstrate here a method that combines a quadratic approximant with a conformal mapping. The mapping forces the approximant to focus only on the singularity structure in one half plane at a time.

A quadratic summation approximant is a function

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

where P_L, Q_M, and R_N are polynomials of degrees L, M, and N, respectively, with the coefficients of the polynomials determined from

$$Q_M \epsilon^2 - P_L \epsilon + R_N \sim \mathcal{O}(z^{L+M+N+2}), \tag{3}$$

where ϵ represents an asymptotic power series for the energy. Eq. (3) leaves one coefficient undetermined. Therefore, we add an additional condition $Q(0) = 1$. To the extent that the approximant models the true functional form of the energy, roots of the discriminant polynomial,

$$D_{[L/M,N]} = P_L^2 - 4Q_M R_N, \tag{4}$$

correspond to locations of branch points of $E_{\text{FCI}}(z)$.

Let the asymptotic series of the FCI energy be

$$E_{\text{FCI}}(z) \sim \sum_{i=0}^{n} E_i z^i, \tag{5}$$

with MP4 given by $n = 4$. E_0 is the sum of Hartree–Fock orbital energies. It is convenient to introduce

$$\epsilon(z) = E_0 + \left[E_{\text{FCI}}(z) - E_0\right]/z, \tag{6}$$

with asymptotic series

$$\epsilon(z) \sim \sum_{i}^{n-1} \epsilon_i z^i, \qquad \epsilon_0 = E_0 + E_1, \qquad \epsilon_{i>0} = E_{i+1}. \tag{7}$$

The zeroth-order coefficient, ϵ_0, is the Hartree–Fock approximation for the total energy. $\epsilon(z)$ has the same singularity structure as E_{FCI}. We have found no advantage to analyzing the original series, Eq. (5). This is presumably because E_0 and E_1 are determined primarily by nonsingular contributions, with no useful information about the singularity structure.

Because Eq. (7) is a series of order $n - 1$, the polynomial indices for MP4 must satisfy the condition $L + M + N = 2$. Otherwise the particular index choice seems to have no significant effect on the accuracy. We will use the index $[1/0, 1]$ in the present analysis, which gives branch points

$$z_1 = \left(\frac{\beta}{\alpha} + 2\gamma\right)^{-1}, \qquad z_2 = \left(\frac{\beta}{\alpha} - 2\gamma\right)^{-1}, \tag{8}$$

$$\alpha = \epsilon_2/\epsilon_1, \qquad \beta = \epsilon_3/\epsilon_1, \qquad \gamma = \left(\beta - \alpha^2\right)^{1/2}. \tag{9}$$

For MP series it is usually the case that $\beta > \alpha^2$, implying that z_p and z_n are pure real. One can expect that the approximant should be unable to fit both the real and imaginary parts of two branch-point pairs, as that would involve determining four numbers using only the three series coefficients, ϵ_1, ϵ_2, and ϵ_3

as input. In practice, the approximant fits a complex-conjugate pair with a single, pure real, point halfway between them. Note that for a geometric series with $E_{i-1}/E_i = r$, we have $\gamma = 0$ and $z_1 = z_2 = r$, which agrees with the prediction of the ratio test. Thus γ takes into account the deviation of low-order series coefficients from simple geometric series behavior.

In order to avoid the problematic situation of singularities in both half planes approximately equidistant from the origin, the bilinear mapping,

$$u(\lambda, z) = \frac{z}{1 - \lambda + \lambda z}, \tag{10}$$

$$z(\lambda, u) = \frac{(1 - \lambda)u}{1 - \lambda u}, \tag{11}$$

will be used to shift the singularity positions. λ is an arbitrary parameter. The fixed points of this mapping are $z = u = 0$ and $z = u = 1$. Varying λ from $-\infty$ to $+\infty$ moves a point in the complex plane along the circle containing the point in question and the two fixed points. The significant singularities of $E_{\text{FCI}}(z)$ typically have a real part less than 0 or greater than 1, with the imaginary part much smaller than the real part. Therefore, positive λ in practice shifts singularities in the positive half plane toward $u = 1$ and singularities in the negative half plane away from $u = 0$. Negative λ does the opposite.

The series coefficients in the u plane are, for $i > 0$,

$$\tilde{\epsilon}_i(\lambda) = \sum_{j=1}^{i} \binom{i-1}{j-1} \lambda^{i-j} (1 - \lambda)^j \epsilon_j \tag{12}$$

with $\tilde{\epsilon}_0 = \epsilon_0$ [32]. One can show [33] that this mapping is essentially equivalent to using the Feenberg repartitioning of the Hamiltonian [34]. However, Feenberg chose the condition $\tilde{\epsilon}_3(\lambda) = 0$ as the criterion for assigning the value of λ. Here, we choose λ so that the branch point of $S_{[1/0,1]}$ that is closest to the origin is an extremum with respect to λ. This choice results in the MP4qλ approximant [16], which has been shown to be an effective method for summing MP4 series [35].

There are two such extrema: λ_{p}, which leads to a branch point u_{p} in the positive half plane, and λ_{n}, which leads to a branch point u_{n} in the negative half plane. They are given by

$$\lambda_{\text{p,n}} = \frac{1}{\alpha - 1} \left[\frac{\gamma}{\gamma \pm (\alpha - 1)} + \alpha \right], \tag{13}$$

with "+" for λ_{p} and "−" for λ_{n}. Eq. (11) yields corresponding branch points in the original z plane,

$$z_{\text{p}} = z(\lambda_{\text{p}}, u_{\text{p}}), \qquad z_{\text{n}} = z(\lambda_{\text{n}}, u_{\text{n}}). \tag{14}$$

The explicit expressions are

$$z_{\text{p,n}} = \left(\alpha + \frac{2\gamma^2}{\alpha - 1} \pm 3\gamma \right)^{-1}, \tag{15}$$

where "+" gives z_{p} and "−" gives z_{n}.

Table 1 compares z_{p} and z_{n} with benchmark branch point positions for a variety of small atoms and molecules. The benchmark values were determined [15] from quadratic approximants

of high-order MP series computed with FCI methodology [8].[2] Also shown are the branch points from the MP4 quadratic approximant for MP4 without the mapping, from Eqs. (8). We refer to this as the MP4q approximant. Both of its singularities lie in the same half plane in all cases. Often, one of these is very far from the origin and seems to have no physical significance. The systems in Table 1 are grouped into classes, as discussed in Ref. [15]. (For example, for a system of class $\beta|\alpha$ the singularities with smallest real parts in the negative and positive half planes are of class β and class α, respectively.) The basis sets are from the families of correlation-consistent sets developed by Dunning [37]. The prefix "aug" indicates that the basis has been augmented with diffuse functions [38].

Although the singularities in the positive half plane are all outside the unit circle, they can significantly slow the convergence of summation approximants for the energy if they are close to the physical point $z = 1$ [16,39]. MP4qλ_{p} gives a reasonable estimate for the real part of the singularity closest to the origin in the positive half plane in almost all cases. The only exceptions are Cl$^-$ and Ar with the compact cc-pVDZ basis set, which for practical purposes are nonsingular, because their singularities are far from $z = 0$ and $z = 1$. MP4qλ_{p} is especially accurate if the true real part is less than 1.5. Otherwise, the worst case is F$^-$ with aug-cc-pVDZ, for which MP4qλ_{p} underestimates the singularity position, probably due to interference from the dominant singularity in the negative half plane, which has an especially large weight [15]. In the least accurate cases (F$^-$, Ne, and Cl$^-$ with aug-cc-pVDZ and HCl with cc-pVDZ) the positive singularity is much more distant than the negative one and should therefore have little effect on summation.

The last column in Table 1 shows the ratio-test estimate, E_3/E_4, of the distance between the dominant singularity and the origin. (The ratio should be negative for a singularity near the negative real axis.) Clearly, the ratio test is not generally reliable for these systems at such low order. Its values are an indication of how far these perturbation series are from their asymptotic limits.

In the negative half plane there is often a singularity within the unit circle, which would cause direct partial summation of the energy—simply adding up subsequent terms—to diverge at high order. (For this reason it is prudent in general to use con-

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[2] The series coefficients used here were computed by Leininger et al. as described in Ref. [8], using the PSI3 software package [36]. The tabulated coefficients in Ref. [8] were truncated at 6 decimal digits. Tables of series coefficients with the full precision of the computation (12 digits past the decimal point), including series for a few additional systems (Ne, Cl$^-$, HCl, and BO$^+$ with the cc-pVDZ basis, and OH$^-$ and SH$^-$ with the aug-cc-pVDZ basis) not included in Ref. [8], were provided to us by Dr. Wesley Allen. The coefficients $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3$ for fourth-order analysis of the additional systems are, for Ne, -182.616100286014, -0.185523281150, -0.002358595941, -0.002393080524; for Cl$^-$, -459.542220318846, -0.134405350425, -0.011848758475, -0.001032616281; for HCl, -460.089433045457, -0.146387976128, -0.015577563996, -0.002713943043; for BO$^+$, -99.030054115982, -0.271838618315, 0.023829776776, -0.045620861630; for OH$^-$, -75.395884323005, -0.241056315219, 0.007632415013, -0.019784643683; for SH$^-$, -398.133595979631, -0.159633804331, -0.016627283826, -0.005562037925.

Table 1

Branch points of the ground-state MP energy function from quadratic approximants. Accurate singularity positions, from Ref. [15], are compared with estimates from fourth-order series [8,36]. MP4 results without conformal mapping are from Eq. (8). MP4qλ results, with conformal mapping, are the values z_n and z_p from Eq. (15)

System (basis)	Negative singularities	Positive singularities	MP4 singularity	MP4qλ singularities	Ratio test
Class $\alpha|\alpha$:					
CN$^+$ (cc-pVDZ)	$-0.68 \pm 0.13i$	$1.07 \pm 0.22i$	$-0.35, -1.33$	$-0.46, 1.08$	-0.56
C$_2$ (cc-pVDZ)	$-0.955 \pm 0.328i$	$1.187 \pm 0.326i$	$-0.33, -0.86$	$-0.52, 1.11$	-0.47
	$-1.57 \pm 0.53i$	$1.76 \pm 0.65i$			
N$_2$ (cc-pVDZ)	$-1.505 \pm 0.638i$	$1.66 \pm 0.32i$	$-0.25, -0.34$	$-0.98, 1.50$	-0.29
Ne (cc-pVDZ)	$-2.62 \pm 0.90i$	$3.14 \pm 0.51i$	$0.81, 1.27$	$-2.84, 3.07$	0.99
Class $\alpha|\beta$:					
Cl$^-$ (cc-pVDZ)	$-2 \pm 5i$	$2.6 \pm 0.1i$	$11 \pm 2i$	$10 \pm 3i$	11.5
	-5.6				
Ar (cc-pVDZ)	$-2 \pm 8i$	3.3	$5.68 \pm 7.54i$	$-0.30 \pm 7.1i$	15.7
		$1.2 \pm 4.0i$			
Class $\beta|\alpha$:					
BO$^+$ (cc-pVDZ)	$-0.5227 \pm 0.0131i$	$1.24 \pm 0.26i$	$-0.37, -0.90$	$-0.63, 1.22$	-0.522
	$-1.2 \pm 0.3i$				
OH$^-$ (aug-cc-pVDZ)	$-0.566 \pm 0.002i$	$1.774 \pm 0.873i$	$-0.32, -0.49$	$-0.96, 1.50$	-0.39
	$-2.0 \pm 0.4i$	$1.863 \pm 0.718i$			
F$^-$ (aug-cc-pVDZ)	$-0.639 \pm 0.008i$	$1.98 \pm 1.02i$	$-0.40, -0.71$	$-0.99, 1.57$	-0.51
HF (aug-cc-pVDZ)	$-0.7595 \pm 0.0149i$	$1.94 \pm 1.04i$	$0.070, 0.073$	$-1.50, 1.94$	0.071
Ne (aug-cc-pVDZ)	$-0.824 \pm 0.007i$	$3.0 \pm 0.6i$	$0.25, 0.30$	$-1.84, 2.23$	0.27
Cl$^-$ (aug-cc-pVDZ)	$-0.980 \pm 0.015i$	$1.980 \pm 0.764i$	$2.06, 51.0$	$-3.31, 2.51$	3.95
	$-0.78 \pm 3.23i$	$2.5 \pm 0.3i$			
HCl (aug-cc-pVDZ)	$-1.13 \pm 0.02i$	$2.20 \pm 0.29i$	$2.15, 559$	$-3.64, 2.39$	4.21
HF (cc-pVDZ)	$-1.28 \pm 0.02i$	$2.4 \pm 0.3i$	$0.57, 0.85$	$-2.18, 2.47$	0.68
HCl (cc-pVDZ)	$-1.49 \pm 0.05i$	$2.23 \pm 0.78i$	$2.91, 231$	$-6.08, 2.90$	5.74
Class $\beta|\beta$:					
SH$^-$ (aug-cc-pVDZ)	$-0.966 \pm 0.005i$	1.86	$1.55, 40.5$	$-2.41, 1.94$	2.99
		$2.1 \pm 0.5i$			
Ar (aug-cc-pVDZ)	-1.244 ± 0.014	2.576	$3.96, 198$	$-8.94, 3.85$	7.76
BH (cc-pVDZ)	-4.0	1.45	$1.60, 11.7$	$-6.09, 1.54$	2.81
		$1.58 \pm 0.25i$			
BH (aug-cc-pVQZ)	-2.08	1.387	$1.27, 2330$	$-2.00, 1.46$	2.53
		$1.67 \pm 0.53i$			
BH (aug-cc-pVTZ)	-2.97	1.42	$1.39, 125$	$-2.54, 1.49$	2.75
	$-2.9 \pm 0.8i$	$1.56 \pm 0.63i$			
BH (cc-pVQZ)	-3.2	1.46	$1.29, 3 \times 10^5$	$-2.07, 1.47$	2.57
		$1.69 \pm 0.53i$			
BH (aug-cc-pVDZ)	-3.03	1.60	$1.56, 13.5$	$-5.19, 1.53$	2.80
		$1.57 \pm 0.48i$			
BH (cc-pVTZ)	$-3.80 \pm 0.08i$	$1.43 \pm 0.05i$	$1.41, 88.9$	$-2.64, 1.49$	2.77
		$1.70 \pm 0.45i$			

vergent summation approximants to evaluate MP energies [10, 16].) A positive class α singularity close to $z = 1$ is generally accompanied by a singularity close to the origin in the negative half plane. In contrast, it is often the case that a negative class β singularity within the unit circle will not be accompanied by a positive class α singularity near $z = 1$. This can occur when the basis set contains diffuse functions, which allow the wavefunction to model the dissociation of the system at the critical point [14] and leads to the dramatic divergence of the high-order series observed by Olsen and coworkers [4]. However, the class β singularity has little effect on the low-order series coefficients, and in such cases the MP4 energy can be summed relatively easily using appropriate approximants [16,35].

While MP4qλ_n gives a lower bound to the position of a dominant negative class β singularity, MP4q gives an upper bound,

due to "attraction" by the singularity in the positive half plane. The approximant attempts to model the positive and negative singularities with a singularity in between them. This is shown in Fig. 1. It is interesting that the average of MP4q and MP4qλ_n (the open circles) gives a much improved estimate of the class β singularity position. To better understand this phenomenon, we reproduce it using a simple model function. Consider

$$f(z) = a_1(1 - z/z_1)^{1/2} + a_1^*\left(1 - z/z_1^*\right)^{1/2}$$
$$+ a_2(1 - z/z_2)^{1/2} + a_2^*\left(1 - z/z_2^*\right)^{1/2}$$
$$+ bw_x e^{c_x z}, \quad (16)$$

which consists of branch points at the dominant singular points of the FCI energy function with an exponential function added to provide a nonsingular contribution to the series. We set the
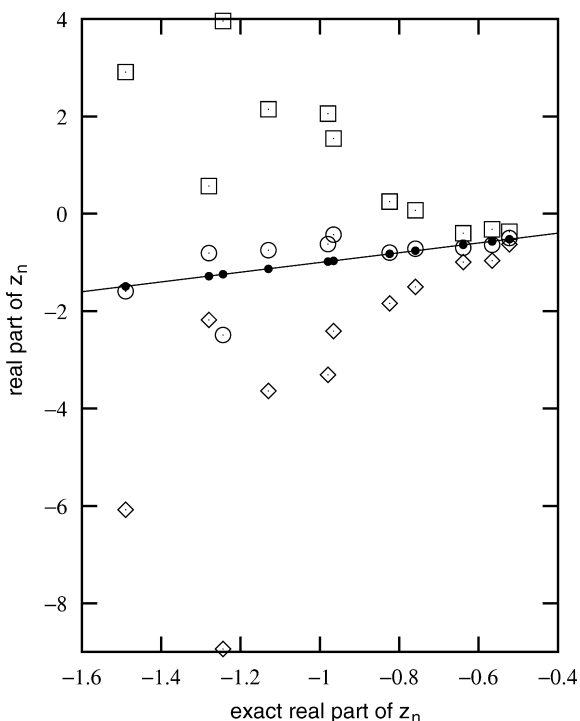
Fig. 1. Real part of the class β singularity in the negative half plane for systems in which this is the dominant singularity. The exact result (filled circles and line) is compared to estimates from the MP4 quadratic approximant (squares), the MP4qλ_n approximant (diamonds), and the average of the two (open circles).
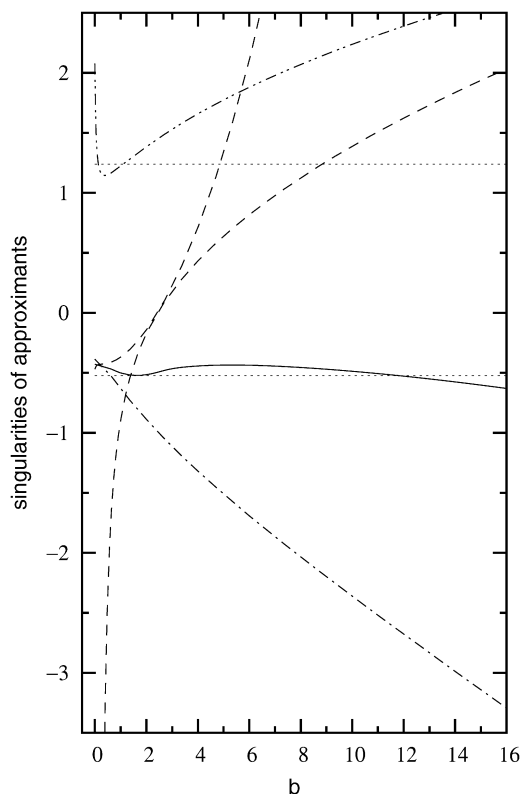

Fig. 2. Singularity analysis of model function $f(z)$ with parameters fit to BO$^+$ (cc-pVDZ): $a_1 = 0.142 + 0.486i$, $z_1 = -0.5227 + 0.0131i$, $a_2 = 0.078 - 0.021i$, $z_2 = 1.24 + 0.26i$, $w_x = -18.3545$, $c_x = 0.228473$. The variable b is the weight of the nonsingular part. $b = 1$ gives the results for the actual MP4 series. The singularity positions from the MP4q, MP4qλ_n, MP4qλ_p approximants are shown by the dashed, dash-dot, and dash-dot-dot curves, respectively. The solid curve shows the average of the MP4qλ_n singularity and the MP4q singular point closest to the origin. The dotted lines show the exact real part of the BO$^+$ singular points.

parameters of the singularities, a_i and z_i, to values determined from quadratic approximant analysis of an actual high-order MP series [15]. Then, letting $b = 1$, we set the parameters w_x and c_x so that the coefficients of the fourth-order Taylor series of $f(z)$ gives values for α and β equal to those for the MP series. Thus, singularity analysis of f with $b = 1$ gives the same singularity positions as does analysis of the corresponding MP4 series. Analysis at $b = 0$ shows how the approximants perform without interference from the nonsingular part.

The various approximants respond differently to the nonsingular contributions. This is illustrated by Fig. 2, which shows the singularity analysis of f with the parameters corresponding to BO$^+$ with the cc-pVDZ basis. The figure shows the effect of increasing the weight factor b of the nonsingular part. The dotted curves show the exact singularity locations. The solid curve shows the average of the MP4qλ_n singularity and the MP4q singular point closest to the origin. Without the exponential (i.e., at $b = 0$), the MP4qλ_n singularity and one of the MP4 singularities model the exact dominant singularity, in the negative half plane, reasonably well while MP4qλ_p places the positive singularity somewhat beyond the exact position. As the nonsingular contribution increases, MP4qλ_p becomes more accurate, as the effect of the dominant singularity is blunted. Eventually, the positive singularity is also masked by the exponential and the MP4qλ_p result moves out from the origin. The masking of the negative singularity has opposite effects on MP4q and MP4qλ_n. The former moves in the positive direction while the latter moves in the negative direction, and the average of the

two is an accurate estimate of the exact position over a wide range of b.

The remarkable stability of this average, despite the divergence of the individual MP4qλ_n and MP4q values, results from the nonsingular contribution masking the singularity in the negative half plane more strongly than the one in the positive half plane. The contributions to the series coefficients $\epsilon_1, \epsilon_2, \epsilon_3$ from the latter singularity are negative while those from the former alternate in sign, with the contribution to ϵ_2 positive. If the singularity in the negative half plane is clearly the dominant one, then $\alpha = \epsilon_2 / \epsilon_1$ is negative. For the cases in which the MP4q, MP4qλ_n average is stable, the nonsingular contribution to ϵ_2 is negative. As b is increased, the effect of the dominant singularity is blunted, with α eventually becoming positive. The MP4q result moves in the positive direction, attracted by the positive singularity as it appears to become dominant. MP4qλ_n, by construction, models a singularity in the negative half plane. It moves away from the origin in the negative direction as the negative half plane appears to become nonsingular. The average is extremely accurate for the first five of the class $\beta|\alpha$ systems, which are distinguished by an α value less than 0.01 and an MP4 value less than 0.5.

The nonsingular effects are qualitatively different when the singularity in the negative half plane is of class α. In such cases, MP4qλ_n is more accurate than the average. The analysis based on a fourth-order series cannot alone always distinguish the cases for which the average is reliable. For example, it can be seen in Table 1 that the MP4 series for OH$^-$ and for N$_2$ yield nearly identical singularities. N$_2$, which has a class α negative singularity, is not accurately modeled by the average. A nonpolar molecule with a compact basis set is expected not to have a dominant negative class β singularity [14]. Knowing this, one can infer that the negative singularity for N$_2$ is of class α and should be described with MP4qλ_n itself rather than the average. At fifth order the two cases are readily distinguished.

MP4 singularity analysis has an immediate practical application. We will show elsewhere that it is reliable enough to enable one to choose an appropriate summation approximant for summing the MP4 series for the energy. Also, the MP4qλ_p singularity position could, in principle, provide a general diagnostic for predicting the accuracy of single-reference state ab initio computations. The class α branch-point pair closest to $z = 1$ describes an avoided crossing between the ground state and the first excited state of the same symmetry. If the branch points are close to $z = 1$, then one can expect strong overlap of the wavefunctions of the two states in the physical solution, at $z = 1$. This would imply that the Hartree–Fock solution is an inappropriate zeroth-order approximation, and would suggest that the Hamiltonian be repartitioned to shift the singularity structure [40,41] or that a more laborious multireference method be used instead [42]. This applies to MP perturbation theory but also to other methods, such as coupled-cluster theory [35,39], that extrapolate from the Hartree–Fock approximation. A class β singularity, if close to the origin, can also affect the accuracy of MP summation approximants, although the effect is usually smaller than that of a class α singularity, and it should not be expected to affect the accuracy of non-MP methods [35].

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