Singularity Analysis of Fourth-Order Møller-Plesset Perturbation Theory

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A method is developed for determining the singularity structure of Møller-Plesset many-body perturbation theory from fourth-order perturbation series, using a quadratic approximant with a bilinear conformal mapping. Optimal mappings are determined from extremum conditions. Comparison with singularity positions determined from high-order series for ground-state energies of atoms and molecules shows that the fourth-order method gives reliable estimates of singularity structure in the positive half plane, which is usually what most affects the accuracy of summation approximants, and reasonable estimates of singularity structure in the negative half plane.

Keywords: many-body perturbation theory, Møller-Plesset perturbation theory, quadratic summation approximants, asymptotic series, singularity analysis

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 taken as the zeroth-order solution for the wavefunction and Rayleigh-Schrödinger perturbation theory is used to determine higher-order corrections. The theory can be formulated from a partitioning of the Hamiltonian [2],

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

in terms of a perturbation parameter z. $H_{\rm phys}$ 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 $z = 1$.

The power series for the energy eigenvalue 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 that there will exist two classes of singularities [3–7]. Class α singularities are complex-conjugate pairs of isolated square-root branch points [3]. They represent avoided crossings of the ground-state energy 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 [4, 6, 7].

The critical points, in principle, are branch points with a complicated functional form [4, 8]. This would be true, at least, if the exact Hartree-Fock wavefunction were used as the zeroth-order solution. In practice, an approximation to the Hartree-Fock solution is used, with the wavefunction approximated 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 eigenvalue equation. This is the *full configuration-interaction* energy, $E_{\rm FCI}(z)$, which can only have square-root branch points, in complex-conjugate pairs off the real axis [3, 8]. Thus, the class α singularities are accurately modeled but the class β singularities are not. In practice, $E_{\rm FCI}(z)$ models a class β critical point of $E(z)$ with a cluster of square-root branch point pairs with very small imaginary parts [6].

In previous work we have studied the singularity structure of $E_{\rm FCI}(z)$ for specific examples from quantum chemistry using two approaches. First, we computed the FCI eigenvalue spectrum for many different values of real z and determined the branch point locations from analysis of the avoided crossings with the ground state [6]. Since each FCI computation is quite costly, this strategy is not very efficient, and the analysis was carried out for only a few different systems. Subsequently, we determined singularity structure for a much larger set of systems by analyzing the high-order behavior of the asymptotic series [9]. The series coefficients can be determined to high order and with high precision using intermediate quantities obtained in the course of an FCI computation [10–14]. Thus, a single FCI computation for $z = 1$ 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 atoms or molecules with no more than approximately 10 correlated electrons. For routine applications one uses the fourth-order Møller-Plesset perturbation theory (MP4), which can be efficiently computed from explicit formulas [2]. The problem we address here is how to locate the singularities of $E_{\rm FCI}(z)$ given only its fourth-order asymptotic series. This order is much too low for standard methods of asymptotic analysis to be of much use. Asymptotic methods such as the D'Alembert ratio test and its more sophisticated variants [15–17] 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 [18], they are not well suited for studying nondominant singularities. The typical sin-

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gularity structure of $E_{\rm FCI}(z)$ for atoms and molecules is to have singularity structure 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 [9].

A more promising strategy is to use an *approximant*, an arbitrary function containing parameters that are fit to the known asymptotic series coefficients of the true function. The advantage of this approach 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 only a small number of parameters. Because we know that the singularities of $E_{\rm FCI}(z)$ are square-root branch points, we can design the approximant accordingly. The straightforward approach for modeling square-root branch points is a quadratic approximant [19, 20]. Unfortunately, for MP4 with complex-conjugate pairs of branch points in both half planes at approximately the same distance from the origin, these approximants attempt to simultaneously model all these singularities with a single branch point close to the origin [21], which is the average of the true singularity positions, and 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. Comparing with the earlier results from high-order series analysis, we find that this strategy at fourth-order in almost all cases gives a reliable estimate for the position of the class α singularity nearest to the origin. In many cases it also gives a reasonable estimate for the location of a second class α singularity or for a class β singularity.

A quadratic summation approximant is a function

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

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

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

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

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

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

Let the asymptotic series of the FCI energy be

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

with order $n = 4$ corresponding to MP4. E_0 is the sum of Hartree-Fock orbital energies. It is convenient to introduce a function

$$\epsilon(z) = E_0 + [E_{\rm FCI}(z) - E_0]/z, \quad (6)$$

with asymptotic series

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

Then the zeroth-order coefficient, ϵ_0, is the Hartree-Fock approximation for the total energy. $\epsilon(z)$ has the same singularity structure as $E_{\rm FCI}$. 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 of the results. We will use the index [1/0,1] in the present analysis, which gives branch points

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

where

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

For MP series it is usually the case that $\beta > \alpha^2$, implying that $z_{\rm p}$ and $z_{\rm n}$ are pure real. 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. The parameter 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,

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

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

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 $E_{\rm FCI}(z)$ typically have a real part that is less than 0 or greater than 1, and the imaginary part is usually 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 $u = 0$, while negative λ does the opposite.

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

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

with $\tilde{\epsilon}_0 = \epsilon_0$ [22]. One can show [23] that this mapping is essentially equivalent to using the Feenberg repartitioning of the Hamiltonian [24]. However, Feenberg chose the condition $\epsilon_3(\lambda) = 0$ 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 [25], which has been shown to be an effective method for summing MP4 series [26].

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

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

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

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

The explicit expressions are

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

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

Table I compares $z_{\rm p}$ and $z_{\rm n}$ with accurate branch point positions for a variety of small atoms and molecules. The accurate values were determined [9] from quadratic approximants of high-order MP series computed with FCI methodology [14, 27]. Also shown branch points from quadratic approximants for MP4 without the mapping, from Eqs. (8). Without the mapping, both 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 I are grouped into classes, as discussed in Ref. 9. For a system of class $\beta\alpha$, for example, 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 [28]. The prefix "aug" indicates that the basis has been augmented with diffuse functions [29].

It is immediately apparent that $z_{\rm p}$ gives a reliable estimate for the real part of the class α singularity closest to the origin in the positive half plane. This is true even when there is a singularity in the negative half plane much closer to the origin. $z_{\rm n}$ gives a reasonable, but less accurate, estimate for a class α singularity in the negative half plane. For those cases in which a class β singularity is the dominant singularity, the MP4qλ singularities are consistently farther from the origin than is the accurate result. This is presumably because the imaginary part of a class β complex conjugate branch-point pair is quite small, making it almost a double root of the discriminant polynomial. The singular nature of the function is not obvious except in the immediate neighborhood of the singular points. At low-order, these singularities have a smaller effect on the series coefficients than might be expected based on their distance from the origin. To the MP4qλ approximant they appear to be farther away than they actually are. While the MP4qλ approximant gives a lower bound to the position of a dominant negative class β singularity, the conventional MP4 approximant gives an upper bound, due to the effect of the singularity in the positive half plane. This is shown in Fig. 1. It is interesting that the average of the MP4 and MP4qλ estimates (the open circles) gives a much improved estimate of the class β singularity position.

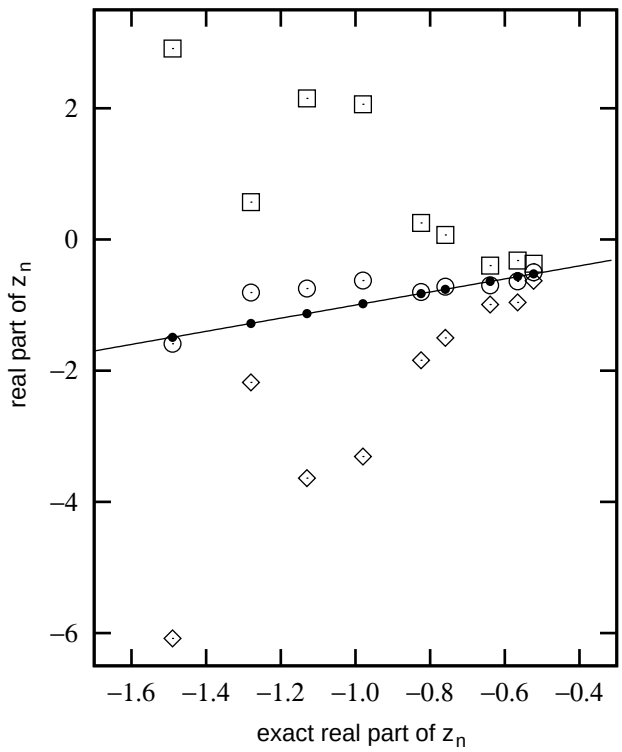

FIG. 1: Real part of class β singularity in negative half plane for systems in Table I for which this is the singularity structure closest to the origin. The exact result (filled circles and line) is compared to estimates from the MP4 quadratic approximant (squares), the MP4qλ approximant (diamonds), and the average of the two (open circles).

It is our hope that singularity estimates from fourth-order series can be used as a diagnostic to predict the accuracy of an *ab initio* computation of the ground-state electronic energy. The class α branch-point pair closest to the physical point describes an avoided crossing between the ground state and the first excited state of the same symmetry. If they are close to the physical

TABLE I: Branch points of the ground-state MP energy function from quadratic approximants. Accurate singularity positions, from Ref. 9, are compared with estimates from fourth-order series. MP4 results without conformal mapping are from Eq. (8). MP4qλ results, with conformal mapping, are the values z_{n} and z_{p} from to Eq. (15).

Class	System (basis)	Negative singularities	Positive singularities	MP4 singularity	MP4qλ singularities
$\alpha\alpha$	CN^+ (cc-pVDZ)	$-0.68 \pm 0.13i$	$1.07 \pm 0.22i$	-0.35, -1.33	-0.46, 1.08
	C_2 (cc-pVDZ)	$-0.955 \pm 0.328i$ $-1.57 \pm 0.53i$	$1.187 \pm 0.326i$ $1.76 \pm 0.65i$	-0.33, -0.86	-0.52, 1.11
	N_2 (cc-pVDZ)	$-1.505 \pm 0.638i$	$1.66 \pm 0.32i$	-0.25, -0.34	-0.98, 1.50
	Ne (cc-pVDZ)	$-2.62 \pm 0.90i$	$3.14 \pm 0.51i$	0.81, 1.27	-2.84, 3.07
$\alpha\beta$	Cl^- (cc-pVDZ)	$-2 \pm 5i$ -5.6	$2.6 \pm 0.1i$	$11 \pm 2i$	$10 \pm 3i$
	Ar (cc-pVDZ)	$-2 \pm 8i$	3.3 $1.2 \pm 4.0i$	$5.68 \pm 7.54i$	$-0.30 \pm 7.1i$
$\beta\alpha$	BO^+ (cc-pVDZ)	$-0.5227 \pm 0.0131i$ $-1.2 \pm 0.3i$	$1.24 \pm 0.26i$	-0.37, -0.90	-0.63, 1.22
	OH^- (aug-cc-pVDZ)	$-0.566 \pm 0.002i$ $-2.0 \pm 0.4i$	$1.774 \pm 0.873i$ $1.863 \pm 0.718i$	-0.32, -0.49	-0.96, 1.50
	F^- (aug-cc-pVDZ)	$-0.639 \pm 0.008i$	$1.98 \pm 1.02i$	-0.40, -0.71	-0.99, 1.57
	HF (aug-cc-pVDZ)	$-0.7595 \pm 0.0149i$	$1.94 \pm 1.04i$	0.070, 0.073	-1.50, 1.94
	Ne (aug-cc-pVDZ)	$-0.824 \pm 0.007i$	$3.0 \pm 0.6i$	0.25, 0.30	-1.84, 2.23
	Cl^- (aug-cc-pVDZ)	$-0.980 \pm 0.015i$ $-0.78 \pm 3.23i$	$1.980 \pm 0.764i$ $2.5 \pm 0.3i$	2.06, 51.0	-3.31, 2.51
	HCl (aug-cc-pVDZ)	$-1.13 \pm 0.02i$	$2.20 \pm 0.29i$	2.15, 559	-3.64, 2.39
	HF (cc-pVDZ)	$-1.28 \pm 0.02i$	$2.4 + 0.3i$	0.57, 0.85	-2.18, 2.47
	HCl (cc-pVDZ)	$-1.49 \pm 0.05i$	$2.23 \pm 0.78i$	2.91, 231	-6.08, 2.90
$\beta\beta$	SH^- (aug-cc-pVDZ)	$-0.966 \pm 0.005i$	1.86 $2.1 \pm 0.5i$	1.55, 40.5	-2.41, 1.94
	Ar (aug-cc-pVDZ)	-1.244 ± 0.014	2.576	3.96, 198	-8.94, 3.85
	BH (cc-pVDZ)	-4.0	1.45 $1.58 \pm 0.25i$	1.60, 11.7	-6.09, 1.54
	BH (aug-cc-pVQZ)	-2.08	1.387 $1.67 \pm 0.53i$	1.27, 2330	-2.00, 1.46
	BH (aug-cc-pVTZ)	-2.97 $-2.9 \pm 0.8i$	1.42 $1.56 \pm 0.63i$	1.39, 125	-2.54, 1.49
	BH (cc-pVQZ)	-3.2	1.46 $1.69 \pm 0.53i$	1.29, 3×10^5	-2.07, 1.47
	BH (aug-cc-pVDZ)	-3.03	1.60 $1.57 \pm 0.48i$	1.56, 13.5	-5.19, 1.53
	BH (cc-pVTZ)	$-3.80 \pm 0.08i$	$1.43 \pm 0.05i$ $1.70 \pm 0.45i$	1.41, 88.9	-2.64, 1.49

point, then one can expect a strong overlap of the wavefunctions of the two states, which would imply that the Hartree-Fock solution is an inappropriate zeroth-order approximation, and would suggest that a more laborious multireference method be used instead. This applies, of course, to MP perturbation theory but also to other methods, such as coupled-cluster theory [26, 30], 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 [26].

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