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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 perturbation 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],

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

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, $E_{\mathrm{FCI}}(z)$, 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, $E_{\mathrm{FCI}}(z)$ 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 $E_{\mathrm{FCI}}(z)$ 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 $E_{\mathrm{FCI}}(z)$ 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 $E_{\mathrm{FCI}}(z)$ 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

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

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 $E_{\mathrm{FCI}}(z)$.

Let the asymptotic series of the FCI energy be

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

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

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

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