

Singularities of Møller-Plesset energy functions

Alexey V. Sergeev^{a)} and David Z. Goodson^{b)}

Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts 02747

(Received 31 October 2005; accepted 19 January 2006; published online 7 March 2006)

The convergence behavior of Møller-Plesset (MP) perturbation series is governed by the singularity structure of the energy, with the energy treated as a function of the perturbation parameter. Singularity locations, determined from quadratic approximant analysis of high-order series, are presented for a variety of atoms and small molecules. These results can be used as benchmarks for understanding the convergence of low-order methods such as MP4 and for developing and testing summation methods that model the singularity structure. The positions and types of singularities confirm previous qualitative predictions based on functional analysis of the Schrödinger equation. © 2006 American Institute of Physics. [DOI: [10.1063/1.2173989](https://doi.org/10.1063/1.2173989)]

I. INTRODUCTION

Møller-Plesset (MP) perturbation theory takes the Hartree-Fock approximation as the zeroth-order solution for the wave function and then uses Rayleigh-Schrödinger perturbation theory to develop a perturbation series to some specified order for the ground-state energy. The fourth-order perturbation theory was formerly considered the method of choice for high-accuracy *ab initio* computations, but on account of concerns raised about the convergence of the perturbation series¹⁻⁷ it has, in recent years, been supplanted by the popular CCSD(T) coupled-cluster theory. Nevertheless, the MP theory has the advantage of a relatively straightforward theoretical foundation. The MP energy can be thought of as an asymptotic series of a function of a perturbation parameter, and as such can be analyzed using methods of functional analysis. Information obtained from this analysis can be used to interpret the results of both MP and CCSD(T) calculations.^{8,9}

The convergence behavior of the energy series can largely be explained in terms of singularity analysis of the energy function in the complex plane of the perturbation parameter.¹⁰⁻¹⁵ In principle, there exist two classes of singularities:^{14,15} Class α singularities are isolated complex-conjugate pairs of square-root branch points, which correspond to the avoided crossings between the ground state and an excited state on a path along the real axis, while class β singularities lie on or near the real axis and correspond to critical points at which one or more electrons dissociate from the nuclei. The behavior of the energy series is determined by the positions of the singularities, by the relative weights of the singularities, and by their classes.

Our purpose here is to present accurate characterizations of the MP singularity structures for a variety of small molecules and atoms with various basis sets. The singularity locations are determined from the analysis of high-order MP

energy series. Many such series are now available in the literature,^{2,4,7} having been computed using a full configuration-interaction (FCI) methodology.¹⁶⁻¹⁸ These singularity structures are intended as benchmarks for evaluating the accuracy of low-order methods of singularity analysis and for validating qualitative principles that have been developed^{5,14,15} for predicting the nature of the dominant singularities.

The various singularity structures found here for different systems fully account for the variety of series convergence behaviors observed by other workers.^{2,4,5,7,19,20} If the closest singularity structure to the origin is in the negative half of the complex plane, then the series coefficients generally alternate in sign, while if it lies in the positive half plane, subsequent series coefficients will generally have the same sign. If the dominant singularity is a complex-conjugate pair with a relatively large imaginary part, then partial sums of the series will show a superimposed oscillation. This accounts for the distinctive “ringing” patterns noted by Leininger *et al.*⁷

Divergent series result from singularity structure within the unit circle. However, as we have emphasized elsewhere,^{12-14,21} the fact that a series diverges does not imply that it is useless. Divergent and slowly convergent MP series can be summed using approximants that model the singularities. These approximants can yield very high accuracy even if the series coefficients are only available through fourth order. A system with an isolated complex-conjugate singularity pair that is much closer to the origin than any other singularities can be accurately modeled by the approximant at low order, even if the conventional partial sums of the series diverge, while convergent series with more complicated singularity structures may require a higher-order series for comparable summation accuracy. The fact that a given series is divergent or convergent is less significant in practice than the question of whether or not the underlying singularity structure is simple enough to be modeled at low order by a summation approximant.

Section II presents a brief review of the MP perturbation equations and a summary of what is known in advance, from

^{a)}Present address: Department of Chemistry, Tulane University, New Orleans, LA.

^{b)}Electronic mail: dgoodson@umassd.edu

functional analysis, about the nature of MP singularities. Our method for extracting singularity positions from high-order series coefficients is described in Sec. III and the results are given in Sec. IV. Then in Sec. V the various systems are classified according to their singularity structures using the “ α, β ” singularity classes proposed in Refs. 14 and 15. Implications of these classifications are discussed.

II. BACKGROUND

The Møller-Plesset partitioning of the Hamiltonian²² can be written as

$$H(z) = H_0 + zH_1, \quad H_1 = H_{\text{phys}} - H_0, \quad (1)$$

where H_{phys} is the exact Schrödinger Hamiltonian and H_0 is the sum of one-electron Fock operators. z is a continuous perturbation parameter that extrapolates between H_0 at $z=0$ and H_{phys} at $z=1$. The eigenfunctions $\Psi^{(i)}$ of $H(z)$ are then expressed as

$$\Psi^{(i)}(z) \sim \sum_{k=0}^n \psi_k^{(i)} z^k, \quad (2)$$

which leads to a power series in z for the ground-state energy eigenvalue,

$$E(z) \sim \sum_{k=0}^n E_k z^k. \quad (3)$$

The finite integer n is the order of the perturbation theory. The $\psi_0^{(i)}$ are the Hartree-Fock determinants. E_0 is the sum of the occupied orbital energies for the ground-state electron configuration. The symbol “ \sim ” means that the left-hand side of the equation is asymptotically equal to the power series in the $z \rightarrow 0$ limit.²³

The formal solutions for the series coefficients E_k for $k > 0$ are

$$E_k = \langle \psi_0^{(0)} | H_1 | \psi_{k-1}^{(0)} \rangle, \quad (4)$$

where the $\psi_k^{(0)}$ are determined by the equation

$$(H_0 - E_0) \psi_k^{(0)} = -H_1 \psi_{k-1}^{(0)} + \sum_{j=1}^k E_j \psi_{k-j}^{(0)}, \quad (5)$$

with $\langle \psi_k^{(0)} | \psi_0^{(0)} \rangle = 0$ for $k \neq 0$. In practice, in order to solve these equations the ψ_k are expressed as linear combinations of products of one-electron atomic basis functions. Equations (4) and (5) can then be interpreted as matrix equations and solved recursively using the $\psi_{j < k}^{(0)}$ to construct the matrix H_1 to be used to determine $\psi_k^{(0)}$.

A straightforward approach to compute high-order series is to take advantage of the FCI methodology.^{16,17} A FCI computation involves the construction of a matrix representation of H_{phys} , which is then diagonalized to determine its eigenvalues. However, if the H_{phys} matrix is available then it can be used to compute the matrix H_1 for use in Eqs. (4) and (5). The LUCIA FCI program^{24,25} and the PSI software package²⁶ have been modified for this purpose and, as a result, MP series to very high order for a variety of atoms and molecules with up to eight correlated electrons are now available.^{2,4,7,27}

From first principles,^{10,14,15,28,29} one can expect two classes of singular points in the function $E(z)$ in the complex z plane. Singularities of class α are isolated square-root branch points corresponding to values of z at which the ground state becomes degenerate with an excited state of the same symmetry. These exist in complex-conjugate pairs, with nonzero imaginary part. Suppose $E(z)$ has class α singularities at the points z_α and z_α^* . Following the energy functions for the two eigenstates along the real axis, an avoided crossing occurs with closest approach at $z = \text{Re } z_\alpha$. Singularities of class β are critical points. They are found on the real axis and correspond to values of z beyond which the lowest-energy eigenstate no longer binds all of the electrons.

The expressing of the ψ_k as linear combinations in a finite-dimension basis set introduces an approximation into the analysis. The perturbation series, Eq. (3), is no longer the asymptotic series of the true energy function $E(z)$ but is now the asymptotic series of the FCI energy function $E_{\text{FCI}}(z)$, which is the energy corresponding to the minimum-energy linear combination of determinants for a given basis, according to the variational principle. The functional forms of $E(z)$ and $E_{\text{FCI}}(z)$ differ in a key respect: Because the Hamiltonian has been approximated with a finite-dimension Hermitian matrix, the eigenvalue functions cannot have singularities on the real axis.^{28,30} It was demonstrated in Ref. 15 that in the vicinity of a critical point of $E(z)$, the corresponding $E_{\text{FCI}}(z)$ will have a grouping of complex-conjugate branch-point pairs with very small imaginary parts, as long as the basis set contains functions that are sufficiently diffuse to model the dissociation.

The behavior of an asymptotic series at high order is determined by the singularity structure closest to the origin, called the dominant singularity. A precise statement of this is provided by a theorem of Darboux.³¹ If a function $f(z)$ has an algebraic singularity at a point z_j , such that in a neighborhood of z_j the function behaves according to the functional form

$$f(z) \sim (1 - z/z_j)^\alpha F(z) + G(z), \quad (6)$$

where $F(z)$ and $G(z)$ are functions that are nonsingular in the disk $z \leq z_j$, then the coefficients f_k of the Taylor series of f about the point $z=0$ asymptotically approach the Taylor series of the function $F(z_j)(1 - z/z_j)^\alpha$. Thus, as the series order increases, the coefficients will contain less and less information about the functional forms of $F(z)$ and $G(z)$ and will be essentially determined just by the three parameters z_j , α , and $F(z_j)$.

MP series have previously been classified according to patterns in the signs of the series coefficients.^{5,19,20,32} Early results suggested that all series fell into either of two categories: either the series coefficients all had the same sign or, starting at least by fourth order, the coefficients alternated in sign.^{32,33} Series with constant sign were designated as belonging to “class A” while those with alternating signs were placed in “class B.” Subsequent studies^{5,7,19,20} suggested that the situation is not so simple. While most series seemed to fall into one of these two classes, some showed more complicated sign patterns.

An immediate consequence of Eq. (6) is that if z_j is on the negative real axis, then the series coefficients at high order alternate in sign, and if z_j lies on the positive real axis, they have the same sign. The analysis is more complicated if the singularity structure consists of a complex-conjugate pair of singularities, as in $E_{\text{FCI}}(z)$. Then the high-order coefficients are given by the Taylor series of the function

$$\phi_j(z) = F(z_j)(1 - z/z_j)^{1/2} + F(z_j^*)(1 - z/z_j^*)^{1/2} \quad (7)$$

(with exponent $\alpha=1/2$, for square-root branch points), which superimposes a sinusoidal oscillation on the sign pattern that would have resulted if the singularity was on the real axis at $z=|z_j|$.³⁴ The Taylor series of ϕ_j is

$$\phi_j(z) \sim \frac{1}{2} |F(z_j)| \sum_{k=0}^{\infty} \binom{1/2}{k} (-1)^k |z_j|^{-k} \cos(\Omega - k\Theta) z^k, \quad (8)$$

where

$$z_j = |z_j| e^{i\Theta}, \quad F(z_j) = |F(z_j)| e^{i\Omega}. \quad (9)$$

This implies that the period of the oscillation is

$$\tau = 2\pi / |\arg(z_j)|. \quad (10)$$

If $|\text{Im } z / \text{Re } z|$ is small, then τ will be large and the series will seem to fall into class A or B, with anomalous behavior evident only at very high order.

Another possible cause of the breakdown of the A/B classification is a situation in which there are singularities in both the positive and negative half planes that are approximately equidistant from the origin. Suppose branch points exist at z_1, z_1^*, z_2 , and z_2^* with $|z_1|$ slightly smaller than $|z_2|$. At extremely high order, the E_k would be dominated by the series coefficients implied by Eq. (7) with $j=1$, but at intermediate orders both singularity pairs could make significant contributions. In general, a more accurate model for the series would come from

$$\Phi(z) = \sum_j \phi_j(z), \quad (11)$$

summed over all significant singularities z_j, z_j^* . The factor of $|z_j|^{-k}$ in Eq. (8) strongly favors the singularities closest to the origin with increasing k . However, it will be demonstrated in Sec. IV that MP series often have a branch-point pair in the negative half plane that is at approximately the same distance from the origin as a branch-point pair in the positive half plane.

Another complication comes from the fact that in the limit $\text{Im } z_1 \rightarrow 0$, the function $\Phi(z)$ of Eq. (11) becomes non-singular at z_1 . Class β singularities of E_{FCI} are expected to have much smaller imaginary parts than are class α singularities. This suggests that the effects at intermediate orders on the series coefficients of a class α singularity at some given distance from the origin could be comparable in magnitude to the effects of a class β singularity that is considerably closer to the origin.

One way to salvage the A/B classification system is to add additional classes to describe the variety of possible patterns in the coefficients.²⁰ However, we prefer the alternative of classifying the series according to the singularity structure

responsible for the series behavior.^{14,15} Let z_n, z_n^* and z_p, z_p^* be the positions of the dominant singularity pair in the negative and positive half planes, respectively. (We refer to the closest singularity to the origin in a given half plane as the dominant singularity in that half plane.) Series will be assigned a singularity class of $\alpha\alpha, \beta\alpha, \alpha\beta$, or $\beta\beta$ according to the class of the dominant singularities; class $\beta\alpha$ means that z_n is of class β while z_p is of class α and so on. The full classification will consist of the singularity class and the values of $-|z_n|$ and $|z_p|$. We will often use the word ‘‘singularity,’’ in the singular, to refer to a class α complex-conjugate pair of singularities or to refer to the whole class β cluster of complex-conjugate singularity pairs with which E_{FCI} models a single critical point of $E(z)$.

III. ANALYSIS OF HIGH-ORDER SERIES

There are two kinds of strategies for extracting information about singularity structure of a function $f(z)$ from its series coefficients f_k .³¹ The first kind includes methods based directly on Darboux’s theorem. An example is the well-known D’Alembert ratio test, using $|f_{k-1}/f_k|$ in the limit of large k as an estimate of the dominant singularity position $|z_s|$. Various other similar but more complicated Darboux-inspired techniques have also been developed.^{31,34} A disadvantage of these methods is that they can converge quite slowly if there is more than one significant singularity. Another disadvantage is inherent in the Darboux theorem—these methods only provide information about the singularity nearest the origin. Conformal mappings can be used to transform an originally nondominant singularity into the dominant one,³¹ but with the complicated singularity structures of MP series we have found Darboux methods with conformal mappings to be impractical. The maximum orders of the available MP series are not high enough.

The second kind of strategy for series analysis is to postulate some functional form, called an ‘‘approximant,’’ containing adjustable parameters. The parameters are then chosen so that the Taylor series of the approximant agrees with the asymptotic series of the actual function up to some specified order. An advantage of approximants over Darboux methods is that it is possible for them to simultaneously model more than one singularity, even if the singularities are at different distances from the origin. Another advantage is that the convergence can be very rapid if the functional form of the approximant is similar to that of the actual function. A disadvantage of approximants is that, except in certain special cases,³⁵ we lack a rigorous theorem for the rate of convergence.

The use of approximants was pioneered by Padé,^{35,36} who examined rational approximants, $S_{[L/M]} = P_L/Q_M$ where P_L and Q_M are polynomials of degrees L and M , respectively, with the polynomial coefficients determined by the linear equation

$$Q_M f - P_L \sim 0. \quad (12)$$

f in Eq. (12) represents the power series asymptotic to some function $f(z)$. The polynomial coefficients are determined by solving the set of simultaneous linear algebraic equations

obtained by collecting terms proportional to given powers of the variable.

It is preferable to base the choice of the functional form on information other than just the series coefficients. In the case of the function E_{FCI} we know from analysis of the eigenvalue equation that its only singularities are square-root branch points.²⁸ The singularities of the rational Padé approximant consist of poles, at the roots Q_M . Although these approximants can model branch points with clusters of poles and zeros,³⁷ it is more efficient to use an approximant that has the kind of singularities the function is known to contain.

Padé³⁶ also proposed basing approximants on algebraic equations of higher degree than Eq. (12). Consider the quadratic equation

$$Q_M f^2 - P_L f + R_N \sim 0, \quad (13)$$

with three polynomials. This yields the approximant

$$S_{[L/M,N]} = \frac{1}{2} \left(\frac{P_L}{Q_M} \pm \frac{1}{Q_M} \sqrt{P_L^2 - 4Q_M R_N} \right), \quad (14)$$

which has square-root branch points, at the roots of the discriminant polynomial

$$D_{[L/M,N]} = P_L^2 - 4Q_M R_N. \quad (15)$$

We will assume that, with increasing series order, the roots will converge to branch points of $E_{\text{FCI}}(z)$. The branch-point weights in Eq. (7) for each branch point z_j can be estimated as

$$F(z_j) = \lim_{z \rightarrow z_j} \frac{1}{2Q_M} \left[(1 - z/z_j)^{-1} D_{[L/M,N]}(z) \right]^{1/2} \quad (16)$$

$$= \frac{1}{2Q_M(z_j)} \left[-z_j D'_{[L/M,N]}(z_j) \right]^{1/2}. \quad (17)$$

The spectrum of FCI eigenvalues for all states with the same symmetry as the ground state can be thought of as a single function $E_{\text{FCI}}(z)$ with a different Riemann sheet for each eigenvalue. The physical eigenvalues are the value of $E_{\text{FCI}}(1)$ on each sheet. Following $E_{\text{FCI}}(z)$ on a path in the complex plane that encircles a branch point causes a transition from one sheet to another.^{14,29} Although the number of branch points in the $[L/M,N]$ quadratic approximant will be the greater of $2L$ and $M+N$, the function $S_{[L/M,N]}(z)$ has only two branches, corresponding to the choice of sign before the square root in Eq. (14). Therefore, the quadratic approximant can simultaneously describe at most two eigenvalues of E_{FCI} . In principle, higher-degree algebraic approximants, from replacing Eq. (13) with, for example, a cubic or quartic polynomial equation, would give a more accurate description of the functional form, but in practice this requires high-precision series coefficients to higher order than is available for MP series.^{38–40} Because the singularities of $E_{\text{FCI}}(z)$ are known to behave as square-root branch points in the neighborhood of a singular point,²⁸ the quadratic approximant should at least be adequate for describing the ground-state Riemann sheet.

Usually, E_0 and E_1 are not presented separately in the literature; only their sum, the Hartree-Fock energy, is given. Although E_0 is not difficult to compute, we have chosen instead simply to analyze the function

$$\epsilon_{\text{FCI}}(z) = E_0 + [E_{\text{FCI}}(z) - E_0]/z, \quad (18)$$

which has the asymptotic series

$$\epsilon_{\text{FCI}}(z) \sim \sum_{k=0}^{n-1} \epsilon_k z^k, \quad (19)$$

where

$$\epsilon_0 = E_0 + E_1, \quad \epsilon_{k>0} = E_{k+1}. \quad (20)$$

ϵ_{FCI} and E_{FCI} have identical singularity structure.

We will compute a sequence of approximants corresponding to increasing order n according to the $[L/M,N]$ index sequence

$$[0/0,0],[0/0,1],[1/0,1],[1/1,1],[1/1,2],\dots \quad (21)$$

Since multiplication of both sides of Eq. (13) by a constant leaves the solutions for P_L , Q_M , and R_N unchanged, a normalization condition is needed, which we choose as $Q_M(0) = 1$. The other parameters of the three polynomials are determined from the solution of the n linear equations implied by Eq. (13), with the asymptotic series of ϵ_{FCI} substituted for f . The index for given order n is determined by

$$L + M + N + 2 = n. \quad (22)$$

IV. RESULTS

Table I shows the convergence of the singularity positions of the quadratic approximants for the MP series of the C_2 molecule with increasing order n . The basis set is the correlation-consistent polarization valence double-zeta (cc-pVDZ) set.⁴¹ This basis is compact, lacking diffuse functions, and the molecule is nonpolar. This implies, according to criteria in Ref. 15, that the dominant singularity in the negative half plane will be of class α . The fact that C_2 is known to have a low-lying excited state of the same ${}^1\Sigma_g^+$ symmetry as the ground state⁴ suggests that the dominant singularity in the positive half plane will also be of class α . These expectations are consistent with the quadratic approximant analysis, which shows in each half plane isolated complex-conjugate branch-point pairs with significant imaginary parts, confirming the classification of this system as $\alpha\alpha$.

The convergence is reasonably steady for the dominant singularity in each half plane, and the branch-point pair closest to the origin shows the fastest convergence. At low orders the approximant ignores the imaginary part and places the singularity on the real axis at a point approximately equal to the actual singularity's real part. As the order increases the imaginary part appears and soon shows convergence to approximately the same decimal place as the real part. The table omits branch points that are much farther from the origin than the convergent points. The positions of such points are highly unstable.

Ultimately, accuracy is limited by effects of the finite precision of the series coefficients. The coefficients, which

TABLE I. Convergence of branch-point locations for C_2 (cc-pVDZ) from quadratic approximants, as function of the order of the perturbation series. A bar over a digit indicates that that digit is uncertain due to roundoff error in the series coefficients. Entries in boldface are the best estimates of the singularity positions, as discussed in the text.

Order	Branch points	
5	-0.773 156	1.697 437
10	-0.829 694±0.402 640i -1.203 496±0.455 615i	1.166 929
15	-0.885 410±0.217 481i -1.084 372±0.581 316i -1.093 789	1.203 357±0.381 290i 2.754 408
20	-0.959 079±0.328 454i -1.528 061±0.345 549i	1.116 688±1.037 42i 1.166 531±0.989 774i 1.216 608±0.335 380i
25	-0.954 785±0.327 867i -1.505 86±0.259 07i -1.653 37	1.067 56, 1.072 41 1.169 639±0.333 424i 1.522 46±0.968 74i
30	-0.955 319±0.328 176i -1.422, -1.461 -1.6201±0.3969i	1.187 23±0.326 70i 1.776±0.610i
31	-0.955 234±0.328 262i -1.264, -1.268 -1.6186±0.3689i	1.186 417±0.326 226i 1.7759±0.6728i
32	-0.955 306±0.328 227i -1.399, -1.425 -1.6220±0.3946i	1.185 77±0.325 39i 1.727±0.827i
33	-0.955 302±0.328 227i -1.3852, -1.409 -1.6201±0.3913i	1.185 72±0.325 26i 1.67±0.84i
34	-0.9551 98±0.328 339i -1.228±0.003i -1.6277±0.3635i	1.186 50±0.326 43i 1.762±0.654i
35	-0.955 381±0.328 114i -1.6044 -1.6643±0.4607i	1.023, 1.024 1.1926±0.3316i 1.70±0.13i
36	-0.955 403±0.328 100i -1.833±0.552i	1.159±0.355i 1.163±0.386i 1.165±0.302i
37	-0.955 432±0.328 037i -1.5818±0.5061i -1.5891 -1.813±0.484i	1.034±0.0003i 1.1935±0.3253i 1.747±0.427i
38	-0.955 441±0.328 046i -1.572±0.525i -1.630 -1.711±0.548i	

TABLE I. (Continued.)

Order	Branch points
39	-0.714 599±0.060 227i -0.714 608±0.060 229i -0.956 12±0.327 67i -1.541±0.342i
40	-0.932±0.770i -0.933±0.772i -0.955 50±0.328 29i -1.590±0.314i

were computed by Leininger *et al.*^{7,27} with the PSI software package,²⁶ have 12 digits past the decimal (in units of E_h). To estimate the effect on the branch-point positions in the approximants of this level of precision in the series coefficients, the approximant analysis was performed ten times with random error of magnitude no greater than $1 \times 10^{-12} E_h$ added to each coefficient and the average deviation in each branch-point position was determined. Digits in Table I with average deviation of at least ± 1 are indicated with a bar.

The most significant effect of random error in the coefficients in this case is not the loss of *precision* in the convergent branch points but rather the generation of spurious branch points, which decrease the *accuracy* of nearby convergent points. Spurious points are usually easy to identify. They are more sensitive to the random error than are convergent points and they typically appear as nearly coincident pairs. Exactly coincident points are a double root of $D_{[L/M,N]}$ and therefore are not singular. Due to the finite order of the perturbation series and the finite numerical precision of the series coefficients, there is sometimes a small separation between the two points. This creates a pair of singular points in the approximant where none should exist. Above 20th order most of the spurious branch points for this case are in nearly coincident pairs. Four actual branch-point pairs of the energy function are being modeled by a sequence of approximants in which the number of branch points is steadily increasing, as the degree of the discriminant polynomial increases with order. These nearly double roots are the approximants' way of using surplus branch points.

The closer these spurious points are to the origin, the stronger their effect on the convergent point. For example, at 39th order the spurious points $-0.71 \pm 0.06i$ are closer to the origin than is the convergent branch-point pair and "push" the convergent pair farther out than it should be. At 34th order the spurious pair $-1.228 \pm 0.003i$, which is farther from the origin than the convergent pair, pushes the convergent pair in. Thus, the convergence patterns of the dominant singularities can be explained, as illustrated by Fig. 1. The distance of the converging points from the optimally converged results is plotted as a function of order. There is reasonably steady exponential convergence of results from approximants with no spurious branch points in the region of the branch point in question. At very high orders, significant spurious points become so prevalent that the approximants become

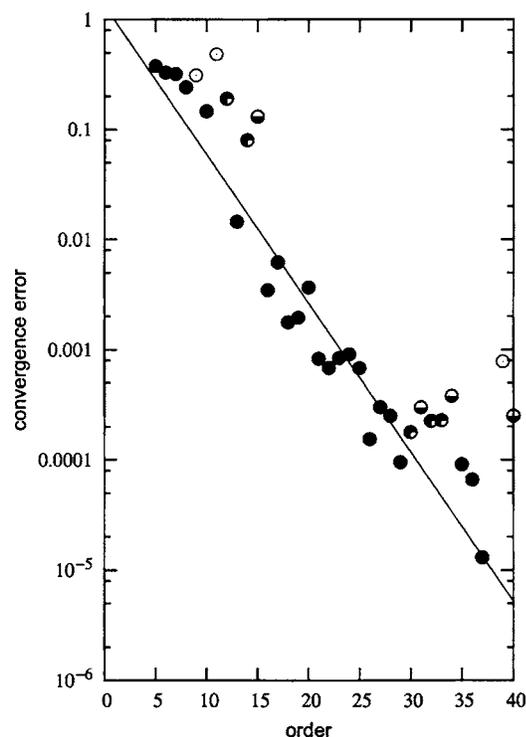


FIG. 1. Error in branch-point convergence, defined as the distance in the complex plane between the dominant branch point of the 38th-order quadratic approximant and the position of the corresponding branch point in the approximant of given order for C_2 (cc-pVDZ). Filled circles are from approximants with no spurious branch points in the region in question. Unfilled circles indicate the presence of spurious branch points in the negative half plane with distance from the origin of less than 1.0 (empty circles), between 1.0 and 1.3 (half filled), and between 1.3 and 1.6 (three-fourths filled). The line shows an exponential fit to the filled circles.

useless. For example, Fig. 2 shows the singularity structure of the approximant at order 47. It is characteristic of these approximants at very high orders that the spurious points are arranged along the unit circle. The highest-order results whose convergence is not affected, indirectly, by spurious branch points or directly by loss of precision are shown in boldface in the table.

Spurious branch points can appear at lower orders due to other causes. In this case, orders 9–15 mark a transition from having one stable branch point in the negative half plane to having two of them, and five of the seven approximants in this range have a spurious branch point. These are isolated points whose positions are unstable from order to order. Once the approximant decides that there is a second, more distant, branch-point pair the spurious singularities disappear.

Table II shows series analysis for Cl^- with the aug-cc-pVDZ basis.⁴² Because the basis is augmented with diffuse functions, this case is predicted to have a class β singularity in the negative half plane. Because chlorine is a highly electronegative element, this singularity is predicted to be the dominant one.¹⁵ The results are as expected. The approximant models a class β singularity with a group of closely spaced branch points on or near the negative real axis, which together presumably models a critical point singularity of $E(z)$ on the real axis. The MP series models $E_{FCI}(z)$, not $E(z)$, and the singularities of E_{FCI} cannot lie on the real axis, al-

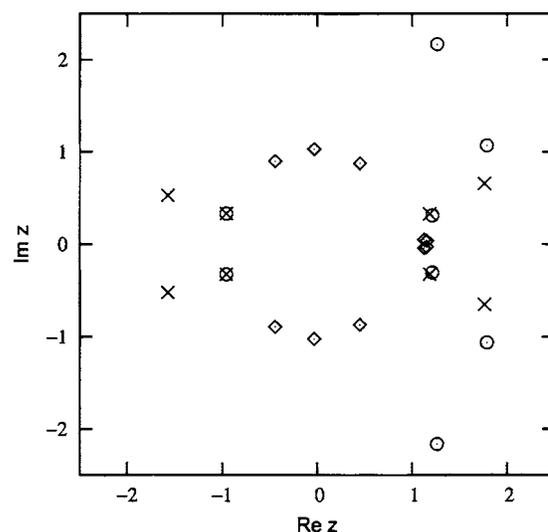


FIG. 2. Branch points of 47th-order quadratic approximant, [15/15,15], for C_2 (cc-pVDZ). The positions of almost double roots (diamonds) and isolated single roots (circles) of the discriminant polynomial are compared with the converged results (\times) from Table I.

though for class β singularities the imaginary parts are expected to be very small. The loss of the imaginary part in the dominant class β singularity at order 24 is presumably a result of the loss of precision in the series coefficients. In addition, there is a class α singularity in the negative half plane and two class α singularities in the positive half plane, all of which are much farther from the origin than is the class β singularity.

For this system what ultimately limits the convergence of the singularity structure is the loss of precision in the branch-point positions. Spurious branch points are less of a problem. The class β singularity structure consists of a cluster of many square-root branch points. Surplus branch points can be utilized productively by modeling this cluster. Furthermore, the propagation of error from the series coefficients to the computed branch points is more severe for branch points that are nearly degenerate. The branch-point positions are determined from the equation $D(z_j)=0$, where D is the computed discriminant polynomial, containing roundoff error δD , and z_j is the computed branch-point position. The error in z_j is

$$\delta z_j \approx -\delta D/D'(z_j). \quad (23)$$

If there is another point very close to z_j that is also a root of D , then $D'(z_j)$ will be small and δz_j will be large. This is consistent with the observed error propagation in Tables I and II. The dominant singularities in the negative half plane for Cl^- and C_2 are at comparable distance from the origin, but Cl^- , with singularity of class β , shows roundoff error in the third decimal place by order 24 while the C_2 singularity, of class α , shows roundoff error in the seventh decimal place at that order.

Table III summarizes the results for a variety of atoms and small molecules for which high-order MP series are available. Only our best estimates of the dominant singularity positions are presented, with the last digit uncertain. The

TABLE II. Convergence of branch-point locations for Cl^- (aug-cc-pVDZ) from quadratic approximants, as function of the order of the perturbation series. A bar over a digit indicates that that digit is uncertain due to roundoff error in the series coefficients. Entries in boldface are the best estimates of the singularity positions, as discussed in the text.

Order	Branch points	
5	-2.990 270	7.568 483
10	-0.985 979 -1.280 154±1.394 014 <i>i</i>	3.817 953
15	-0.932 912 -1.531 289 -0.893 462±1.914 513 <i>i</i>	1.319 814±1.350 375 <i>i</i> 1.453 106±1.109 123 <i>i</i>
20	-0.957 97±0.043 60 <i>i</i> -1.034 50 -0.8058±3.5872 <i>i</i>	2.176 51±0.613 04 <i>i</i>
21	-0.974 41±0.025 63 <i>i</i> -1.076 93 -0.743±2.927 <i>i</i>	1.9711±0.7773 <i>i</i> 2.5659
22	-0.974 37±0.025 34 <i>i</i> -1.076 57 -0.636±3.007 <i>i</i>	1.865±0.662 <i>i</i> 2.23±0.18 <i>i</i>
23	-0.9802±0.0152<i>i</i> -1.096	2.017±0.755 <i>i</i> 3.13±0.50 <i>i</i>
24	-0.963 -1.06 -1.07 -1.11±0.08 <i>i</i> -0.78±3.23<i>i</i>	1.980±0.764<i>i</i> 2.68
25	-0.982 -0.985 -1.111	1.99±0.70 <i>i</i> 2.5±0.3<i>i</i>
26	-0.977 -0.991 -1.115	1.3 1.3 1.99±0.60 <i>i</i>

weight factor for each singularity was calculated using Eq. (17). All of the molecules are at their equilibrium internuclear distances.

V. DISCUSSION

A. Accuracy of results

The singularity locations given in Table III can serve as benchmarks for future studies of MP series summation. In Ref. 15 we presented results for a few of the systems considered here (Ne, Ar, and HF) and compared them to the results of direct computations of the corresponding avoided crossings. For the direct computations, we carried out many FCI computations at different values of z in the neighborhood of the closest approach of the lowest two energy levels and then fitted the cubic approximants to the two energy

curves. This procedure is more laborious than the MP series analysis, which requires only a single FCI computation, but it is presumably more accurate. The results from both methods were in excellent agreement. For class α singularities any disagreement was only in the last digit, while for some of the class β singularities the direct result was slightly closer to the origin than that from the series analysis. The worst case was Ar (cc-pVDZ), for which the direct results was $2.8\pm 0.02i$ compared to our present result of 3.3.

In general, the closer a singularity is to the origin of the complex plane, the faster the convergence of its position in the quadratic approximants of the MP series. The rate of convergence is sometimes unsteady, with sudden jumps to higher accuracy. When there is a pair of nearby singularities the tendency is for the approximant to at first model the two singularities with a single branch point between them. In particular, a complex-conjugate pair will at first be modeled with a branch point on the real axis with an approximately correct real part. The jump in accuracy occurs when the approximant “decides” to use two separate branch points to model the singularity structure instead of just one. In practice the accuracy of the results was in most cases ultimately limited by the finite precision of the series coefficients. Once the increasing effects of this propagation of roundoff error matched the decreasing convergence error, it was useless to continue the analysis to higher orders.

For a given distance from the origin, a dominant class β singularity position will converge more slowly than the position of a dominant class α singularity. This is because an isolated singularity can be modeled by the approximant even at rather low order while two nearby singularities can be distinguished from each other only at higher order. A class β singularity is inherently close to its complex-conjugate partner, because of its small imaginary part, and close to other class β singularities in the cluster that is needed to model a critical point.

In Table III the convergence of the singularity positions is indicated by the number of digits. The last digit in the real part and in the imaginary part of each branch-point position is uncertain. The convergence of the weight factor $F(z_i)$ is somewhat less steady than that of the corresponding singularity position z_i . In most cases we have given the $F(z_i)$ value from the same order as used for the z_i value. In a few cases the effect at this order of roundoff error in the series coefficients caused all digits of $F(z_i)$ to be insignificant. In such cases, the $F(z_i)$ value was taken from a lower-order approximant.

B. Effect of singularities on perturbation series

Convergent results for singularities in both half planes were found for all but two systems. (With the cc-pVDZ basis, the singularities in the negative half plane for Cl^- and Ar are so distant that the convergence is suspect.) The closest singularity to the origin completely determines the high-order series behavior, but singularities more distant from the origin can have an effect at lower orders. This is illustrated by Fig. 3 for the C_2 molecule with the cc-pVDZ basis set. The convergence of partial summation of the energy, from

TABLE III. Branch-point locations from analysis of quadratic approximants. If all the available series coefficients were used, then the order is given in parentheses. When two orders are given, the first corresponds to the singularity position while the second corresponds to the weight. The basis sets are from the cc-pVXZ and aug-cc-pVXZ correlation-consistent families. (Refs. 41–43).

Class	System (basis)	Dominant negative singularity	Weight	Order	Dominant positive singularity	Weight	Order
$\alpha\alpha$	CN ⁺ (cc-pVDZ)	$-0.68\pm 0.13i$	$0.40\pm 0.25i$	(13)	$1.07\pm 0.22i$	$0.038\pm 0.264i$	(13)
	C ₂ (cc-pVDZ)	$-0.955\ 44\pm 0.328\ 05i$	$0.573\pm 0.602i$	38	$1.1865\pm 0.3264i$	$0.303\mp 0.163i$	34
		$-1.57\pm 0.53i$	$1.23\mp 0.48i$	38	$1.76\pm 0.65i$	$0.010\pm 0.137i$	34
	N ₂ (cc-pVDZ)	$-1.505\pm 0.638i$	$0.057\mp 0.727i$	18	$1.66\pm 0.32i$	$0.114\mp 0.129i$	17
	Ne (cc-pVDZ)	$-2.62\pm 0.90i$	$0.4\pm 0.5i$	19	$3.14\pm 0.51i$	$0.06\pm 0.62i$	18
$\alpha\beta$	Cl ⁻ (cc-pVDZ)	$-2\pm 5i$	$0.2\pm 0.2i$	17	$2.6\pm 0.1i$	$0.077\mp 0.036i$	18
		-5.6	0.037	15			
	Ar (cc-pVDZ)	$-2\pm 8i$	$0.7\mp 0.1i$	15	3.3	28	14
				$1.2\pm 4.0i$	$0.41\mp 0.01i$	15	
$\beta\alpha$	BO ⁺ (cc-pVDZ)	$-0.5227\pm 0.0131i$	$0.142\pm 0.486i$	22	$1.24\pm 0.26i$	$0.078\mp 0.021i$	(23)
		$-1.2\pm 0.3i$	$0.02\pm 0.14i$	(23)			
	OH ⁻ (aug-cc-pVDZ)	$-0.566\pm 0.002i$	$0.003\ 28\pm 0.003\ 42i$	25	$1.774\pm 0.873i$	$0.0272\mp 0.0289i$	(27)
		$-2.0\pm 0.4i$	$0.07\mp 0.11i$	25	$1.863\pm 0.718i$	$0.0355\pm 0.0203i$	(27)
	F ⁻ (aug-cc-pVDZ)	$-0.639\pm 0.008i$	$0.295\mp 0.445i$	(21)	$1.98\pm 1.02i$	$0.153\mp 0.056i$	(21)
	HF (aug-cc-pVDZ)	$-0.7595\pm 0.0149i$	$0.000\ 196\pm 0.000\ 359i$	26	$1.94\pm 1.04i$	$0.0134\mp 0.0074i$	25
	Ne (aug-cc-pVDZ)	$-0.824\pm 0.007i$	$0.0032\pm 0.0102i$	35	$3.0\pm 0.6i$	$0.40\pm 0.56i$	21
	Cl ⁻ (aug-cc-pVDZ)	$-0.980\pm 0.015i$	$0.0018\pm 0.0272i$	23,22	$1.980\pm 0.764i$	$0.0432\mp 0.0022i$	24
		$-0.78\pm 3.23i$	$0.046\mp 0.020i$	24,22	$2.5\pm 0.3i$	$0.12\pm 0.03i$	25
	HCl (aug-cc-pVDZ)	$-1.13\pm 0.02i$	$0.000\ 44\pm 0.000\ 50i$	24,21	$2.20\pm 0.29i$	$0.053\mp 0.004i$	23
	HF (cc-pVDZ)	$-1.28\pm 0.02i$	$0.001\pm 0.001i$	21,19	$2.4\pm 0.3i$	$0.2\pm 0.6i$	22,19
	HCl (cc-pVDZ)	$-1.49\pm 0.05i$	$0.0012\pm 0.0017i$	22	$2.2\pm 0.8i$	$0.1\pm 0.02i$	20
	$\beta\beta$	SH ⁻ (aug-cc-pVDZ)	$-0.968\pm 0.016i$	$0.000\ 52\pm 0.000\ 56i$	24	1.86	0.016
Ar (aug-cc-pVDZ)		-1.244 ± 0.014	$0.000\ 84\pm 0.000\ 89i$	20	2.576	0.23	21
BH (cc-pVDZ)		-4.0	0.0015	17	1.45	0.0105	(29)
					$1.58\pm 0.25i$	$0.048\pm 0.036i$	(29)
BH (aug-cc-pVQZ)		$-2.03\pm 0.04i$	$0.001\ 89\pm 0.001\ 87i$	19	1.387	0.028	25
					$1.67\pm 0.53i$	$0.016\mp 0.064i$	25
BH (aug-cc-pVTZ)		-2.97	0.0052	19	1.42	0.024	24
					$1.56\pm 0.63i$	$0.006\mp 0.015i$	24,23
BH (cc-pVQZ)		$-3.06\pm 0.07i$	$0.017\pm 0.017i$	18	$1.39\pm 0.04i$	$0.034\mp 0.030i$	18
					$1.73\pm 0.46i$	$0.29\pm 0.18i$	18,17
BH (aug-cc-pVDZ)		-3.03	0.025	18	1.60	0.19	19
					$1.57\pm 0.48i$	$0.11\pm 0.04i$	19
BH (cc-pVTZ)		$-3.80\pm 0.08i$	$0.10\pm 0.10i$	16	$1.43\pm 0.05i$	$0.038\mp 0.031i$	18
				$1.70\pm 0.45i$	$0.07\pm 0.34i$	17,16	

Eq. (3) with $z=1$, is compared with the convergence at $z=1$ of the Taylor series of the model function $\Phi(z)$ of Eq. (11) with one, two, or three complex-conjugate singularity pairs.

The high-order behavior in this case is completely accounted for by just the singularity pair at $-0.955\ 44\pm 0.328\ 05i$, using only the singularity location and the value of the prefactor. Note the periodic oscillation, consistent with the value $\tau=19.0$ predicted by Eq. (10). Including in addition the singularities at $1.1865\pm 0.3264i$ significantly improves the model at orders 4, 5, and 6, as shown in Fig. 4, but not at higher orders. Including the singularities at $-1.57\pm 0.53i$ only improves the model at fourth order. There is no significant contribution from the singularities at $1.76\pm 0.65i$. Of course, practical applications usually use series at only fourth or fifth order. Figure 4 suggests that accurate summation at fourth order will require modeling of sin-

gularities in both the positive and negative half planes. Below fourth order, it is clear that nonsingular contributions must also be taken into account to accurately describe the series behavior.

Figure 5 compares the high-order behavior for Cl⁻ (aug-cc-pVDZ) with that predicted by the dominant singularity at $-0.980\pm 0.015i$. The singularity structure for this system is clearly dominated by a class β singularity in the negative half plane, which is much closer to the origin than any other singularities. The series shows the expected alternation in signs of the series coefficients, which is modeled quite well by this one singularity pair. Figure 6 shows the results at low orders. The singularity appears to have essentially no effect on the series at orders 2 and 3 and only a small effect at fourth order.

In principle, the fact that singularity effects are relatively insignificant at very low orders might suggest that MP2

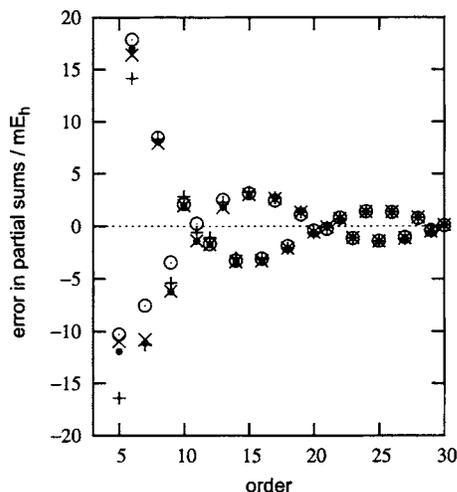


FIG. 3. High-order convergence of C_2 (cc-pVDZ) energy series compared with convergence of model functions consisting only of singularities. Open circles show the error in the MP energy sum, defined as the difference between the partial sum and the FCI energy. The corresponding summation error for the model function for one, two, and three singularities, respectively, is indicated by +, \times , and filled circles.

could give reasonable results even in cases where the series is strongly divergent. An extreme example of this is F^- with the aug-cc-pVDZ basis, which has a class β singularity rather close to the origin and a relatively large value for the real part of the corresponding weight factor. MP4 in this case is less accurate than MP2. The MP4 partial sums differ from the FCI energy by $5.5 mE_h$ while MP2 is in error by only $3.4 mE_h$.

C. Singularity classes

Based on the theoretical expectations summarized in Sec. II and the computed results in Table III, the following generalizations can be inferred for atoms and diatomic molecules.

- (1) The dominant singularity in the negative half plane for atoms and for homonuclear diatomics will be of class α

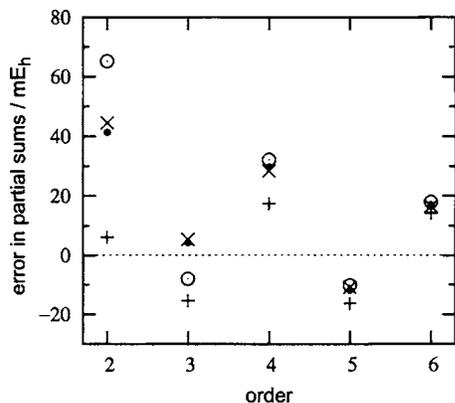


FIG. 4. Low-order convergence of C_2 (cc-pVDZ) energy series compared with convergence of model functions consisting only of singularities. Open circles show the error in the MP energy sum, defined as the difference between the partial sum and the FCI energy. The corresponding summation error for the model function for one, two, and three singularities, respectively, is indicated by +, \times , and filled circles.

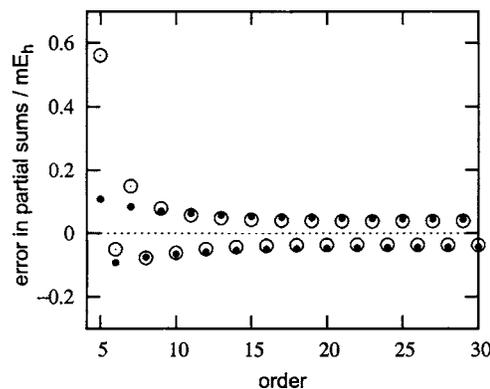


FIG. 5. High-order convergence of Cl^- (aug-cc-pVDZ) energy series compared with convergence of a model functions consisting only of the dominant singularity. Open circles show the error in the MP energy sum, defined as the difference between the partial sum and the FCI energy. The corresponding summation error for the model function is indicated by the filled circles.

if the basis set lacks diffuse functions and of class β if it includes diffuse functions.

- (2) For heteronuclear diatomics the dominant singularity in the negative half plane will be of class β ; adding diffuse functions to the basis moves this singularity closer to the origin.
- (3) Systems with a low-lying excited state that mixes strongly with the ground state, such that a single-reference Hartree-Fock determinant gives a poor description of the wave function, will have a class α singularity in the positive half plane slightly beyond the physical point $z=1$ and a class α singularity in the negative half plane relatively close to the origin.

Class β singularities can be thought of as critical points in an (E, z) phase diagram.^{10,15,29} The system can bind all the electrons only over a certain range of z . As z passes beyond the singularity, it becomes possible for electrons to tunnel out of the confining potential energy well. If the basis set is of the aug-cc-pVXZ type, which is augmented with diffuse functions, then at the critical point all of the valence electrons dissociate from the system. The cc-pVXZ sets, which

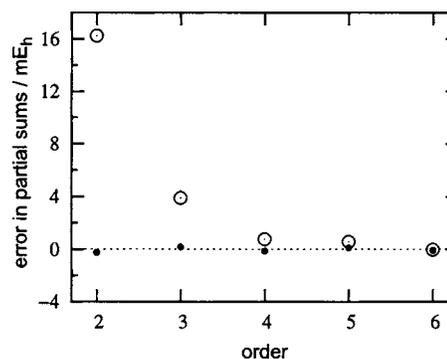


FIG. 6. Low-order convergence of Cl^- (aug-cc-pVDZ) energy series compared with convergence of a model functions consisting only of the dominant singularity. Open circles show the error in the MP energy sum, defined as the difference between the partial sum and the FCI energy. The corresponding summation error for the model function is indicated by the filled circles.

lack diffuse functions, are too compact to model the free valence electrons. However, for heteronuclear diatomic molecules, basis functions centered on the less electronegative atom can model a sudden migration of electrons from one atom to the other.¹⁵ In Table III all the systems with augmented basis sets and almost all the heteronuclear diatomics with compact basis sets have a class β singularity as the dominant singularity in the negative half plane. CN⁺ (cc-pVDZ) is apparently the only exception. This may be due to the relatively small electronegativity difference between C and N causing the critical point to be farther from the origin than a class α avoided crossing.

Some of the systems considered here also show a class β singularity in the positive half plane, which represents a sharp curve crossing of the ground state with either a singly ionized state or a highly excited Rydberg state. The existence of such singularities was conjectured in Ref. 15. Systems with the second-row elements S, Cl, and Ar seem to have such singularities at $z > 1.8$. These are sufficiently distant from the origin that they will have little effect on MP energy series summation. However, BH has a class β singularity in the positive half plane that is relatively close to the origin and is responsible for the slow convergence⁷ of the energy series for this system. This singularity was missed in our previous analysis of the BH series¹⁴ because it is masked at lower orders by a nearby class α singularity.

A class α singularity in the positive half plane represents a qualitative change in the nature of the wave function. Consider a case in which the Hartree-Fock ($z=0$) ground-state wave function is a singlet state with all electrons in doubly occupied orbitals while the first excited singlet state has two singly occupied orbitals. As z increases past 1 on the real axis, the perturbation operator, which includes dynamic electron correlation, increases in importance, according to Eq. (1). Because the correlation is more important for a pair of electrons in the same orbital, the ground-state energy will increase relative to that of the excited state, leading to an avoided crossing and a corresponding complex-conjugate branch-point pair with real part at the point of closest approach. The presence of a class α singularity close to the physical point $z=1$ implies that the Hartree-Fock reference determinant is a qualitatively inaccurate model for the physical wave function. Thus, the position of this singularity can serve as a diagnostic for any method that interpolates between the Hartree-Fock approximation and the FCI solution, including coupled-cluster methods.

A few systems do not fit well into this singularity classification system. With the cc-pVDZ basis, Ne, Cl⁻, and Ar have all their singularities so far from the origin that the singularity structure is of little practical significance. For these systems the MP series are rapidly convergent. For example, the MP4 energy for Ne (cc-pVDZ) differs from the FCI energy by only 0.025 mE_h. This is more accurate than CCSD(T) and it is not improved by summation methods that model the singularity structure.⁸ For BH the singularity structure in the negative half plane is significantly farther from the origin than that in the positive half plane. Although classed as $\beta\beta$ in Table III, the negative β singularity is less important for summation purposes than is the subdominant α

singularity in the positive half plane. These systems could be better described with a designation such as class xx for Ne (cc-pVDZ) and class $x|\beta\alpha$ for BH, where x indicates the absence of significant singularity structure.

The relation between MP singularity structure and the accuracy of summation approximants for MP4 will be examined in detail in a future publication. As an example, we note that for BH the partial summation of the MP series (i.e., simply adding together the series coefficients, in the conventional manner) gives an error of 5 mE_h at fourth order, while the MP4- $q\lambda$ quadratic approximant^{8,21} is very accurate, with summation error on the order of 0.1 mE_h. This is because the singularity structure of the MP4- $q\lambda$ approximant consists of a single square-root branch point on the real axis. Thus it accurately models the dominant singularity of BH. The approximant has no singularity structure in the negative half plane, but because the true singularities of BH in the negative half plane are so much farther from the origin than are those in the positive half plane, this is not a problem. By fitting a single parameter, the pure real position of the one important class β singularity, the approximant accurately characterizes the energy function. In contrast, N₂ is problematic for fourth-order summation approximants, even though its dominant singularity is at about the same distance from the origin as that of BH. To characterize the N₂ energy function the approximant must fit four parameters, the real and imaginary parts of two equally important singularities in both half planes. This requires more information than is available at just fourth order.

ACKNOWLEDGMENT

We thank Dr. Wesley Allen for providing us with unpublished tables of series coefficients with more significant figures than listed in Ref. 7.

- ¹K. A. Peterson and T. H. Dunning, Jr., *J. Phys. Chem.* **99**, 3898 (1995).
- ²O. Christiansen, J. Olsen, P. Jørgensen, H. Koch, and P.-A. Malmqvist, *Chem. Phys. Lett.* **261**, 369 (1996).
- ³J. Olsen, P. Jørgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **105**, 5082 (1996).
- ⁴J. Olsen, O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **105**, 5082 (1996).
- ⁵D. Cremer and Z. He, *J. Phys. Chem.* **100**, 6173 (1996).
- ⁶T. H. Dunning, Jr. and K. A. Peterson, *J. Chem. Phys.* **108**, 4761 (1998).
- ⁷M. Leininger, W. D. Allen, H. F. Schaefer III, and C. D. Sherrill, *J. Chem. Phys.* **112**, 9213 (2000).
- ⁸D. Z. Goodson, *J. Chem. Phys.* **116**, 6948 (2002).
- ⁹D. Z. Goodson and M. Zheng, *Chem. Phys. Lett.* **365**, 396 (2003).
- ¹⁰F. H. Stillinger, *J. Chem. Phys.* **112**, 9711 (2000).
- ¹¹J. Olsen, P. Jørgensen, T. Helgaker, and O. Christiansen, *J. Chem. Phys.* **112**, 9736 (2000).
- ¹²D. Z. Goodson, *J. Chem. Phys.* **112**, 4901 (2000).
- ¹³D. Z. Goodson, *Int. J. Quantum Chem.* **92**, 35 (2003).
- ¹⁴D. Z. Goodson and A. V. Sergeev, *Adv. Quantum Chem.* **47**, 193 (2004).
- ¹⁵A. V. Sergeev, D. Z. Goodson, S. E. Wheeler, and W. D. Allen, *J. Chem. Phys.* **123**, 064105 (2005).
- ¹⁶P. J. Knowles, K. Somasundram, N. C. Handy, and K. Hirao, *Chem. Phys. Lett.* **113**, 87 (1985).
- ¹⁷W. D. Laidig, G. Fitzgerald, and R. J. Bartlett, *Chem. Phys. Lett.* **113**, 151 (1985).
- ¹⁸N. C. Handy, in *Relativistic and Electron Correlation Effects in Molecules*, edited by G. L. Malli (Plenum, New York, 1994), pp. 133–160.
- ¹⁹Z. He and D. Cremer, *Int. J. Quantum Chem.* **59**, 71 (1996).
- ²⁰B. Forsberg, Z. He, Y. He, and D. Cremer, *Int. J. Quantum Chem.* **76**, 306 (2000).

- ²¹D. Z. Goodson, J. Chem. Phys. **113**, 6461 (2000).
- ²²C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
- ²³C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978), pp. 89–90.
- ²⁴J. Olsen, H. Larsen, and M. Fülischer, LUCIA, a full CI restricted active space CI program, University of Aarhus, Aarhus, Denmark, 2002.
- ²⁵J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa. Jensen, J. Chem. Phys. **89**, 2185 (1988).
- ²⁶T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, psi, Version 3.2, 2003, www.psiicode.org
- ²⁷In Ref. 7 the tabulated series coefficients were truncated at six 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. 7, were provided to us by Dr. Wesley Allen.
- ²⁸A. Katz, Nucl. Phys. **29**, 353 (1962).
- ²⁹G. A. Baker, Jr., Rev. Mod. Phys. **43**, 479 (1971).
- ³⁰J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).
- ³¹C. J. Pearce, Adv. Phys. **27**, 89 (1978).
- ³²C. Schmidt, M. Warken, and N. C. Handy, Chem. Phys. Lett. **211**, 272 (1993).
- ³³N. C. Handy, P. J. Knowles, and K. Somasundram, Theor. Chim. Acta **68**, 87 (1985).
- ³⁴C. Hunter and B. Guerrieri, SIAM J. Appl. Math. **39**, 248 (1980).
- ³⁵G. A. Baker, Jr. and P. Graves-Morris, *Padé Approximants* (Cambridge University Press, Cambridge, 1996).
- ³⁶H. Padé, Ann. de l'Ecole Normale Sup., 3ième Série **9**, **Suppl.**, 1 (1892).
- ³⁷G. A. Baker, Jr., *The Essentials of Padé Approximants* (Academic, New York, 1975).
- ³⁸P. G. Drazin and Y. Tourigny, SIAM J. Appl. Math. **56**, 1 (1996).
- ³⁹A. V. Sergeev and D. Z. Goodson, J. Phys. A **31**, 4301 (1998).
- ⁴⁰F. M. Fernández and R. H. Tipping, J. Mol. Struct.: THEOCHEM **488**, 157 (1999).
- ⁴¹T. H. Dunning, Jr., J. Chem. Phys. **53**, 2823 (1970).
- ⁴²R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- ⁴³T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).