

Singularity Structure of Møller-Plesset Perturbation Theory*

David Z. Goodson and Alexey V. Sergeev
Department of Chemistry and Biochemistry
University of Massachusetts Dartmouth
North Dartmouth, MA 02747, USA

April 8, 2004

Abstract

Møller-Plesset perturbation theory expresses the energy as a function $E(z)$ of a perturbation parameter, z . This function contains singular points in the complex z -plane that affect the convergence of the perturbation series. A review is given of what is known in advance about the singularity structure of $E(z)$ from functional analysis of the Schrödinger equation, and of techniques for empirically analyzing the singularity structure using large-order perturbation series. The physical significance of the singularities is discussed. They fall into two classes, which behave differently in response to changes in basis set or molecular geometry. One class consists of complex-conjugate square-root branch points that connect the ground state to a low-lying excited state. The other class consists of a critical point on the negative real z -axis, corresponding to a dissociation phenomenon. These two kinds of singularities are characterized and contrasted using quadratic summation approximants. A new classification scheme for Møller-Plesset perturbation series is proposed, based on the relative positions in the z -plane of the two classes of singularities. Possible applications of this singularity analysis to practical problems in quantum chemistry are described.

*This article is dedicated to Osvaldo Goscinski in recognition of his fundamental contributions to quantum chemistry.

Contents

1	Introduction	2
2	Functional Analysis of the Energy	4
2.1	Singularities of the Energy Function	4
2.2	Convergence Classes	6
3	Extracting Singularity Structure from Perturbation Series	8
4	Examples	11
4.1	Class A	11
4.2	Class B	13
4.3	Systems with Complicated Singularity Structure	14
5	Discussion	15

1 Introduction

The starting point for most *ab initio* calculations of molecular energies is the Hartree-Fock (HF) approximation. Therefore, a central problem of quantum chemistry is the construction of an extrapolation from the HF energy to the true energy eigenvalue of the Schrödinger equation. A particularly straightforward approach, at least in principle, is a perturbation theory proposed by Møller and Plesset [1] in which the HF wavefunction is taken as the zeroth-order approximation for the eigenfunction. The theory can be formulated by partitioning the Hamiltonian according to [2]

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

where H_0 is the sum of one-electron Fock operators, H_{phys} is the Schrödinger Hamiltonian, and z is a perturbation parameter. The energy is then obtained as a power series $E(z) = E_0 + E_1z + E_2z^2 + \dots$. Thus, in Møller-Plesset (MP) theory the energy is a function of z , in the complex z -plane, such that $E(0)$ is equal to the sum of HF orbital energies and $E(1)$ is the extrapolation to the physical energy.

Traditionally, $E(z)$ is calculated by partial summation, that is, the power series is truncated at some given order and then evaluated at $z = 1$. Truncation at order n yields the “MP n ” approximation to the energy. Thus, $E(z)$ is

evaluated as a polynomial. The power series is an asymptotic series, which is a rigorously correct solution only in the $z \rightarrow 0$ limit [3]. The true functional form of E is much more complicated than a polynomial. In particular, it has a rich structure of singular points, that is, points in an infinitesimal neighborhood of which the first derivative does not exist. Since a polynomial is a functional form that is nonsingular at any finite z , it cannot describe the true function in the neighborhood of a singularity or outside the convergence radius determined by the nearest singularity to the origin. This is the cause of poor convergence seen in recent high-order MP n studies [4, 5, 6].

Knowledge of the singularity structure of $E(z)$ can be used to predict the convergence behavior of an MP series [7, 8, 9]. The singularity positions in the MP energy function also affect the convergence of the corresponding coupled-cluster (CC) sequence [10, 11]. Since CC theory is another method that extrapolates from the HF approximation to the exact solution, this is not surprising. Although the function $E(z)$ corresponds to the ground state energy, its singularity structure contains information about excited states. If the singularities are not all reasonably far from the points $z = 0$ and $z = 1$, then this indicates that a single-determinant HF wavefunction will not be a suitable starting point for describing the true wavefunction.

Our purpose here is to review what is known in advance about the functional form of $E(z)$ and then to describe methods for obtaining detailed information about the singularities from analysis of MP series. In Section 2 we present existence theorems that tell us what singularity structure to expect. Then in Section 3 we describe methods for “empirical” studies in which information about singularity structure is extracted from high-order series obtained from full configuration-interaction (FCI) calculations. In Section 4 we analyze some representative examples and clarify the connection between singularity structure and convergence “class.” MP series convergence is often described in terms of a classification scheme developed by Schmidt *et al.* [12]. Series with monotonic convergence are put in class A while series in which the E_i alternate in sign are put in class B. We suggest a modified classification scheme that explains the behavior of molecules with triple bonds or with distorted geometries, which have previously been considered anomalous [5, 6, 13]. Finally, we discuss possible applications of MP singularity analysis to practical problems in quantum chemistry.

2 Functional Analysis of the Energy

2.1 Singularities of the Energy Function

MP perturbation theory is generally used only for the ground state energy. The zeroth-order approximation for the wavefunction is taken to be the lowest-energy HF determinant. Nevertheless, the function $E(z)$ obtained from this perturbation series, when considered as a function over the complex z plane, contains within it the full energy spectrum of eigenstates with the same symmetry as the ground state. This is the consequence of a theorem presented by Katz [14]:

Let $E^{(0)}, E^{(1)}, E^{(2)}, \dots$ be the spectrum of energy functions of Eq. (1) corresponding to a given set of all conserved quantities (e.g., angular momentum). For any i and j there exist complex-conjugate pairs of branch points z_{ij}, z_{ij}^ in the complex z plane at which $E^{(i)}$ is equal to $E^{(j)}$. In the neighborhood of z_{ij}*

$$E^{(i)}(z) = b_{ij} - c_{ij}(1 - z/z_{ij})^{1/2}, \quad E^{(j)}(z) = b_{ij} + c_{ij}(1 - z/z_{ij})^{1/2}, \quad (2)$$

where b_{ij} and c_{ij} are constants, and similarly for z_{ij}^* .

Now consider the ground state function $E^{(0)}(z)$. Starting at the origin, trace a path in the z plane that circles about the point z_{01} . This point is a branch point singularity, which means that a 360° circuit will lead to a new Riemann sheet corresponding to the function $E^{(1)}(z)$. Similarly, following $E^{(0)}(z)$ on a path that circles z_{02} leads to $E^{(2)}(z)$, and so on.

This phenomenon was studied by Baker [15] using a model two-body problem for which an exact solution for $E(z)$ can be obtained. Depending on the choice of parameters, the complex-conjugate branch points connecting $E^{(0)}$ and $E^{(1)}$ could be in the negative half-plane or in the positive half-plane. If branch cuts were specified from these branch points out to infinity, then there were no other branch points. However, if the branch cut was drawn perpendicular to the real axis, joining the two points, then some of the other branch points predicted by Katz, connecting the ground state with higher excited states, were found. The situation is shown schematically in Fig. 1. If one follows $E^{(0)}(z)$ on a path from the origin along the real axis, there will be an avoided crossing as z passes between the 0-1 branch points and no additional avoided crossings with higher states. However, a path that temporarily leaves the real axis to avoid the 0-1 branch points will show no

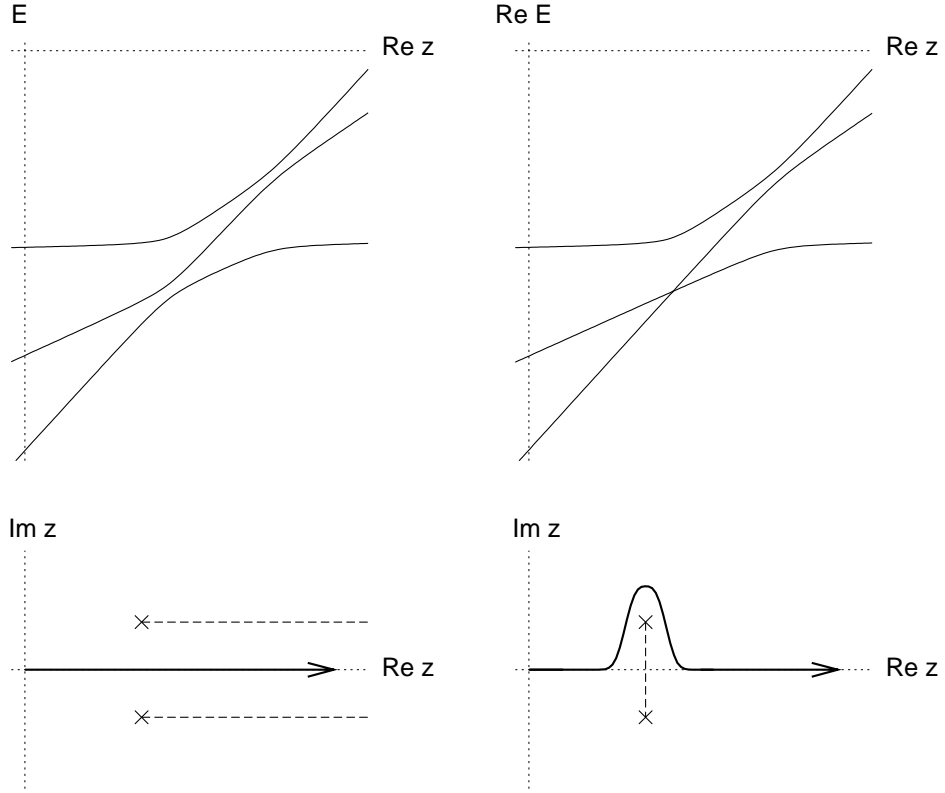


Figure 1: Schematic representation of energy functions $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$ for two paths in the complex z -plane. Branch cuts (dashed lines) are shown for the branch points z_{01} and z_{01}^* .

interaction between $E^{(0)}$ and $E^{(1)}$ but will have an avoided crossing with $E^{(2)}$. Since Katz's analysis does not depend on the specific form of the potential energy function, we expect this behavior to be generic.

These square-root branch points are not the only kind of singularities in the energy function. Baker [15] noted that a many-fermion system in which there are both attractive and repulsive terms in the potential will undergo a spontaneous autoionization at some point on the real z axis. He suggested this is analogous to a critical point in an (E, z) phase diagram. For z beyond the critical value z_c , there can be no eigenstate in which the system is bound. z_c is a branch-point singularity, although presumably of a more complicated

form than Eq. (2). This was studied by Stillinger [16] for the specific case of an atom. He noted that a negative real z , in Eq. (1), implies that the r_{12}^{-1} interelectron potential energy terms in H_{phys} are negative, and hence electrons are mutually attractive. At the same time the repulsive mean field central potential in H_0 is, on the negative real axis, increased by a factor of $(1 + |z|)$, which works against the nucleus-electron attraction. For sufficiently large $|z|$ it will be the case that a bound electron cluster infinitely separated from the nucleus will have a lower energy than any state in which the nucleus is bound. Thus, at z_c the nucleus separates from the atom.

The effect of z_c on the behavior of $E^{(0)}(z)$ on the real axis will be rather different from that of the Katz singularities. On a path from the origin along the negative real axis $E^{(0)}(z)$ acquires an imaginary part as it passes through the singularity. This is because the eigenstate then corresponds to a state in the scattering continuum. We expect that the derivative of the function along this path will be continuous.¹ This is due to the fact that when z is only slightly beyond the critical point there exists a long-range tunneling barrier in the potential, which yields an exponentially small resonance width. Similar behavior is seen in the $1/Z$ expansion, where Z is the nuclear charge, for the two-electron atom [17].

2.2 Convergence Classes

It is common practice to classify MP series in terms of their convergence patterns. With class A systems the E_i series coefficients are all of the same sign. The series show monotonic but often rather slow convergence. Class B series, except at the lowest orders, have E_i that alternate in sign. They often converge rapidly but sometimes diverge. A physical interpretation of this classification system was developed by Cremer and He [13]. They examined the terms in the wavefunction that lead to the sign patterns in the E_i and concluded that the class B sign alternation is caused by orbital crowding, as in systems with highly electronegative atoms and closed shells, while class A behavior results from uncrowded orbitals, as in alkanes and radicals.²

In Ref. [7] it was suggested that these two convergence patterns could

¹The discontinuity of the derivative occurs on paths through z_c that leave the real axis.

²Cremer and coworkers [18] have recently proposed a new nomenclature in which the former classes A and B are now referred to as type I and II, respectively, based on the orbital structure, and with class designations A through E describing a variety of actual convergence patterns seen in practice.

be explained in terms of singularity structure. The sign alternation seen for class B would result if the dominant singularity lies on the negative real axis, while class A would result if the dominant singularity is on the positive real axis. The former is consistent with the Stillinger critical point. The Katz analysis predicts complex-conjugate pairs of branch points displaced from the real axis. This would seem to be inconsistent with the class A sign pattern, since a complex conjugate pair, z_{01}, z_{01}^* in the positive half plane will give a periodic sign pattern with regions in which successive E_i are negative alternating with regions in which they are positive. However, if the imaginary part of these singularities is small then the period, given by [17, 19]

$$n_0 = \pi / \arctan(|\text{Im } z_{01} / \text{Re } z_{01}|), \quad (3)$$

will be sufficiently large that the series will appear to converge monotonically up to very high orders.

A connection between singularity analysis and the Cremer-He analysis can perhaps be made as follows. If the valence electron orbitals are crowded into a relatively small region of space, then the attractive interaction between the electrons (for negative z) is especially strong, as is the mean-field repulsive perturbation. Both of these effects favor autoionization at small $|z|$. It is not surprising that of the class B systems for which high-order MP series have been calculated, the one with the dominant singularity closest to the origin is F^- , with the aug-cc-pVDZ basis set.

It is interesting that the position of z_c is strongly dependent on the basis set. In the case of F^- if the cc-pVDZ basis, which lacks the diffuse functions of the augmented basis sets, is used instead, then the singularity on the negative real axis seems to disappear [5, 7, 20]. Apparently, diffuse functions are needed to describe the autoionization.

In contrast, the position of the dominant singularity for class A systems is relatively insensitive to the basis set. This is a Katz branch point pair connecting the ground state with the first excited state. The interaction between these two states can be described reasonably well with a small basis set. The effect of additional polarization functions, representing highly excited configurations, is small. However, changes in molecular geometries can have a large effect on the class A singularity [11], with bond stretching causing the branch points to move in toward the physical point $z = 1$. The distance of these branch points from $z = 1$ is related to the energy gap between the states at $z = 1$. As a bond is stretched the energy gap decreases and the point of avoided crossing along the positive real axis moves closer to $z = 1$.

It is important to note that a path along the *negative* real axis could also show an avoided crossing between the ground state and the first excited state. Below, in Section 4.3, we present empirical evidence indicating that such a Katz branch point pair, in the negative half plane, is responsible for the worst examples of MP series divergence. Thus, there are two distinct kinds of class B systems. We suggest that classic class B behavior, with alternating signs in the E_i , is due to a critical point while the complicated sign patterns in systems such as the C_2 molecule or in molecules with bonds stretched well beyond the equilibrium distance are due to the simultaneous effects of Katz degeneracies in both the positive and negative half planes.

3 Extracting Singularity Structure from Perturbation Series

There are two general approaches for obtaining information about singularity structure from a perturbation series [21]: asymptotic methods and approximant methods. The former category includes such familiar procedures as the ratio test and the n th-root test as well as some more modern techniques [22, 23], all of which are based on a theorem of Darboux that states that in the limit of large order the series coefficients of the function in question become equivalent to the corresponding coefficients of the Taylor series of the *dominant* singularity, that is, the singularity closest to the origin. The advantage of these methods is that we have for them rigorous convergence proofs. A disadvantage is that they only provide information about the one singularity closest to the origin. More distant singularities can sometimes be studied using conformal mappings [21], but, even for the dominant singularity, convergence can be significantly slowed by interference from other singularities.

For analysis of MP series we have found approximant methods to be more useful than asymptotic methods. The idea is to construct a model function (a *summation approximant*) containing parameters that are chosen so that its Taylor series agrees with the coefficients of the perturbation series up to some given order. Although there are no generally applicable convergence theorems for approximants, if the functional form of the approximant is a reasonable model for the true functional form then the convergence can be rapid. Approximants can simultaneously fit more than one singularity. Fur-

thermore, they provide an analytical continuation to regions of the complex plane where partial sums are poorly convergent or divergent.

A systematic approach to constructing approximants was proposed by Padé [24, 25]. A set of polynomials $A_k^{(m)}(z)$, where k indicates the degree of the polynomial, is defined by the asymptotic relation

$$\sum_{m=0}^M A_{k_m}^m E^m = \mathcal{O}(z^K), \quad K = M + \sum_{m=0}^M k_m. \quad (4)$$

The notation $\mathcal{O}(z^K)$ means that the coefficients of the Taylor series of the left-hand side are equal to zero up through order $K - 1$. E in Eq. (4) represents the perturbation series of the energy function. Collecting terms according to the power of z yields K linear equations for the $K + 1$ coefficients of the polynomials. The final coefficient is set according to an arbitrary normalization condition, typically, $A^{(M)}(0) = 1$. Once the polynomial coefficients are obtained, Eq. (4) is solved for $E(z)$.

With $M = 1$ we have rational approximants, $E(z) = A^{(1)}(z)/A^{(0)}(z)$. The application of these to perturbation theories of the Schrödinger equation was pioneered by Brandäs and Goscinski [26]. They proposed using approximants to determine singularity positions. However, the singularity structure of rational approximants is not of the form we expect for the MP energy. They are single-valued functions, containing poles, at the zeros of $A^{(0)}$, but no branch points. Given enough series coefficients, they can model a branch cut with combinations of poles and zeros [7, 27] but they cannot model more than one branch.

More appropriate are quadratic approximants [7, 27, 28, 29, 30, 31, 32], with $M = 2$, which have the double-valued solution

$$E = \frac{1}{2} \left[\frac{A^{(1)}}{A^{(2)}} \pm \frac{1}{A^{(2)}} \sqrt{(A^{(1)})^2 - 4A^{(0)}A^{(2)}} \right], \quad (5)$$

with a square-root branch point as specified by the Katz theorem. It has two branches (\pm) connected by branch points at the values of z at which the discriminant polynomial, $(A^{(1)})^2 - 4A^{(0)}A^{(2)}$, is zero. In principle, one branch describes the ground state and the other, the first excited state. More complicated branch points are in practice fit by these approximants with clusters of square-root branch points. Approximants with $M > 2$ can describe additional branches of the function, although the accuracy for higher branches tends to be poor unless the series is known to quite high order [33, 34, 35, 36].

Differential approximants, with the powers of E in Eq. (4) replaced by derivatives, can describe a wider variety of singularity types [25, 37].

Other kinds of approximants can also be used. For example, Olsen *et al.* [20] analyzed MP series convergence using a 2×2 matrix eigenvalue equation [38, 39], which implicitly incorporates a square-root branch point. It is of course possible simply to explicitly construct an approximant as an arbitrary function with the singularity structure that $E(z)$ is expected to have. We suggest, for example, approximants of the form³

$$E(z) = \pm P_A(z) [(1 - z/z_{01})(1 - z/z_{01}^*)]^{1/2} + P_B(z)B(z - z_c) + P_C(z), \quad (6)$$

where P_A , P_B , and P_C are polynomials and

$$B(z) = \int_0^\infty (1 + zt)^{3/2} e^{-t} dt, \quad (7)$$

The function $B(z - z_c)$, which can be expressed in terms of an exponential integral, has the behavior we expect for autoionization in that it has a branch point at z_c at which the function becomes complex but with the derivative continuous along the real axis. The coefficients of the polynomials can be chosen so that the Taylor series agrees with the perturbation series.

Note that the gap between the energy of the ground state and that of the first excited state is given by

$$E^{(+)} - E^{(-)} = 2P_A(z) [(1 - z/z_{01})(1 - z/z_{01}^*)]^{1/2}. \quad (8)$$

The value of the gap at $z = 0$ is simply $2P_A(0)$. Since $z = 0$ corresponds to the Hartree-Fock solution, this value is easily calculated. By thus constraining P_A , we can include in the analysis additional information about the singularity structure beyond the information we obtain from the perturbation series. The quadratic approximant, Eq. (5), can be similarly constrained.

At present, the highest order for which direct calculations of MP series have been carried out is only six [40]. However, MP series to arbitrary order can be computed from elements of the Hamiltonian matrix that are obtained in the course of an FCI calculation [41, 42]. As a result, high-order MP series are now available in the literature for a variety of systems with as many as 10 correlated valence electrons [5, 6]. In principle, the singularity structure of $E(z)$ can be obtained from an FCI calculation directly, without calculating the perturbation series, by analyzing the characteristic polynomial as a

³This is an example of an Hermite-Padé approximant [27].

Table 1: Singularity analysis of the energy function of the BH molecule from quadratic approximants. The “weight” corresponds to $|c_{ij}|$ of Eq. (2).

Basis set	Branch point in positive half-plane	Weight	Branch point in negative half-plane	Weight
cc-pVDZ	$1.65 \pm 0.43i$	0.4	-3.6	0.001
cc-pVTZ	$1.60 \pm 0.40i$	0.3	-3.5	0.01
cc-pVQZ	$1.60 \pm 0.31i$	0.4	-3.5	0.04
aug-cc-pVDZ	$1.55 \pm 0.41i$	0.1	-2.5	0.001
aug-cc-pVTZ	$1.59 \pm 0.36i$	0.4	-3	0.01
aug-cc-pVQZ	$1.61 \pm 0.35i$	0.4	-2.1	0.002

function of z . This is a polynomial of very high degree, which makes a full numerical analysis of the z dependence difficult. However, given an initial estimate of a singularity position one could refine the result with a local analysis of the characteristic polynomial in the neighborhood of that point.

4 Examples

4.1 Class A

Consider the molecule BH. Since the boron atom is four electrons short of a full octet, this should be a clear example of class A according to the Cremer-He criteria [13]. The MP series has been calculated [5, 6] through about 15th order for several of the correlation-consistent basis sets [43] and all the E_i have the same sign.

In principle, the zeros of the discriminant polynomial in Eq. (5) correspond to branch points of $E(z)$. Since the number of zeros increases rapidly with the order of the series, we expect most of these branch points to be spurious, and in practice most are unstable from order to order and are often quite distant from the origin or appear as nearly coincident pairs. For BH, the branch points that are stable from order to order are shown in Table 1. They are consistent with the predictions of the functional analysis, with a complex-conjugate pair z_{01}, z_{01}^* with positive real part and a negative real z_c . The former are the dominant singularities, as expected for a class A sys-

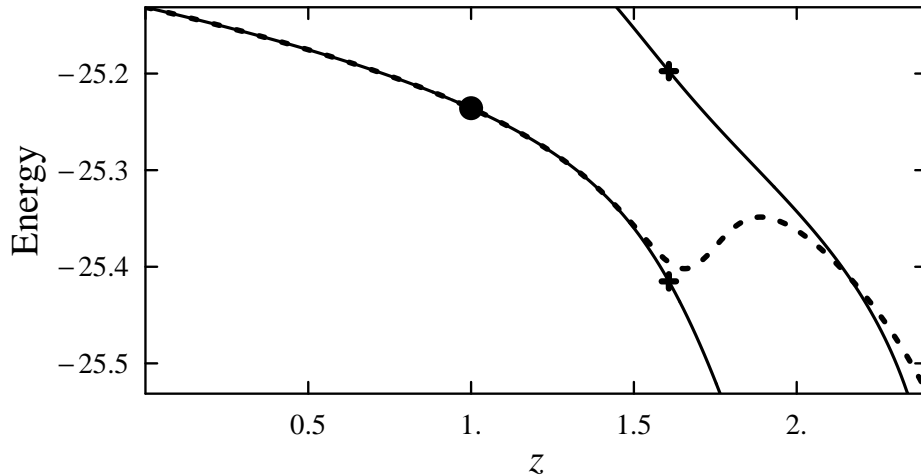


Figure 2: Energy[44] in E_h for BH with the aug-cc-pVQZ basis as a function of real z , from MP series of Leininger *et al.* [6]. The solid curves are the two branches of the quadratic approximant with polynomial degrees 5, 5, and 5, with the values corresponding to the real part of the branch points marked by crosses. The dashed curve is from the rational approximant with degrees 8 and 8. The filled circle shows the physical point.

tem. The z_{01} values imply that the period of the sign pattern of the E_i is somewhere between 13 and 17. Since the highest-order coefficients probably contain significant roundoff error, these values are not inconsistent with the lack of apparent sign alternation in the series. The basis sets represent two families, cc-pVXZ and aug-cc-pVXZ. These are equivalent except that the latter are augmented with diffuse functions. The presence of diffuse functions seems to shift z_c toward the origin but has little effect on z_{01} .

In Fig. 2 we plot the two branches of a quadratic approximant as a function of z on the real axis, for BH with the largest basis set. A broad avoided crossing can be seen at $\text{Re } z_{01}$. Also shown is the result from a rational approximant, which agrees very well with the quadratic approximant for the lower branch up to the avoided crossing. It then jumps to the higher branch after passing through the branch cut between z_{01} and z_{01}^* . Very similar behavior is seen with the other five basis sets.

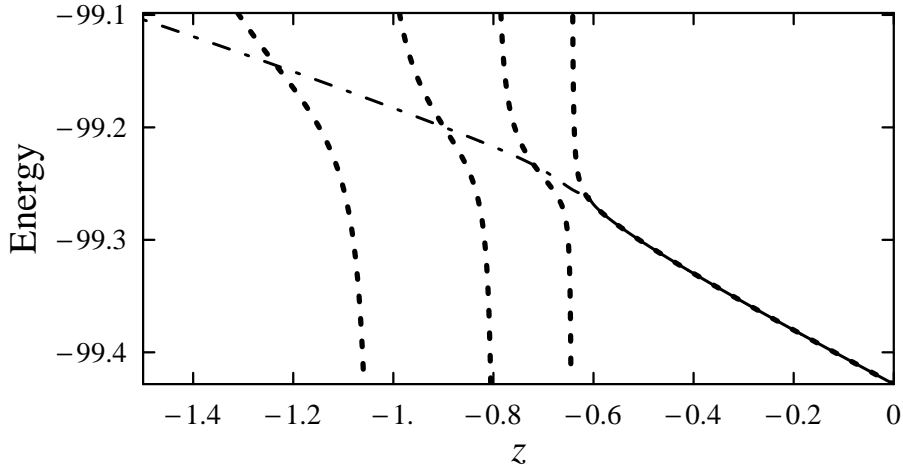


Figure 3: Energy[44] in E_h for F^- with the aug-cc-pVDZ basis as a function of real z , from MP series of Ref. [5]. The solid curve is the quadratic approximant with degrees 6, 6, and 6. When this approximant is complex, the real part is shown as the dash-dot curve. The dashed curve is the rational approximant with degree 9 for the numerator and 10 for the denominator.

4.2 Class B

In Table 1 we also list a singularity for BH on the negative real axis, which presumably corresponds to the critical point. However, the convergence is rather poor since it is much farther from the origin than are the dominant singularities. For a better example we consider the class B system F^- . Christiansen *et al.* [5] found that the MP series for F^- with the aug-cc-pVDZ basis is divergent. The only stable branch point from quadratic approximants is at -0.60 , which presumably corresponds to the critical point, z_c .

Figure 3 shows $E(z)$ for negative real z . Up until z_c the rational and quadratic approximants are in agreement. After passing through z_c the quadratic approximant gains an imaginary part. The rational approximant, unable to produce a branch point, instead maps out a branch cut with alternating poles and zeros [27] along the real axis starting slightly beyond z_c .

In Section 2.1 we argued that for a path along the real axis the derivative at z_c should be continuous. By construction, the singularity from a quadratic approximant is a square-root branch point, of the form $P(z_c)(1 - z/z_c)^{1/2}$

where P is nonsingular at z_c . This expression has a discontinuous derivative along any path. However, the quadratic approximant in Fig. 3 restricts the effects of this discontinuity to the immediate neighborhood of z_c by making the weight of the singularity, $|P(z_c)|$, rather small, in this case, 0.03. For this reason, the discontinuity of the derivative is apparent only on close examination of the curve. Similar behavior is seen for z_c of BH, in which case, as shown in Table 1, the weight of z_c is significantly smaller than the weight of z_{01} . Additional evidence for a qualitative difference between the singularity on the negative real axis and the complex-conjugate pair in the positive half-plane is the fact that the quadratic approximants show more clustering of spurious branch points around the former, suggesting that isolated square-root branch points are insufficient to accurately model the function.

4.3 Systems with Complicated Singularity Structure

Molecules such as N_2 , C_2 , and CN^+ , and in general molecules with bonds stretched from the equilibrium geometry, do not fit well into the A/B classification scheme [5, 6, 13, 20, 40]. They show irregularities in the sign patterns and poor convergence. This has been attributed to the presence of significant singularity structure in both half-planes [7, 9, 10].

For C_2 , quadratic approximants show stable branch points at $1.23 \pm 0.35i$ and $-0.95 \pm 0.33i$. The behavior of $E(z)$ in the vicinity of these points is shown in Fig. 4. It is qualitatively similar to the behavior at z_{01} for BH. In the case of C_2 we see no singularity on the negative real axis. This may be due to the fact that the basis set (cc-pVDZ) lacks diffuse functions.

The anomalous systems have in common a relatively small weight for the Hartree-Fock reference determinant in the $z = 1$ wavefunction, which suggests that Katz branch points will be especially significant. Stretching a bond decreases the energy gap, which shifts avoided crossings to lower values of $|z|$, causing branch point positions to vary significantly along the potential energy surface. Olsen *et al.* [20] found that the negative real singularity for the hydrogen fluoride molecule, determined from the large-order series, also shifts toward the origin as the bond is stretched, but the effect is small. An analysis [11] of MP4 series found a significant shift of singularities toward $z = 1$ in the positive half-plane and toward $z = 0$ in the negative half-plane as the distances increase toward dissociation. The MP4 analysis could not determine the imaginary part of the singular points, and therefore could not distinguish the nature of the singularity in the negative half-plane.

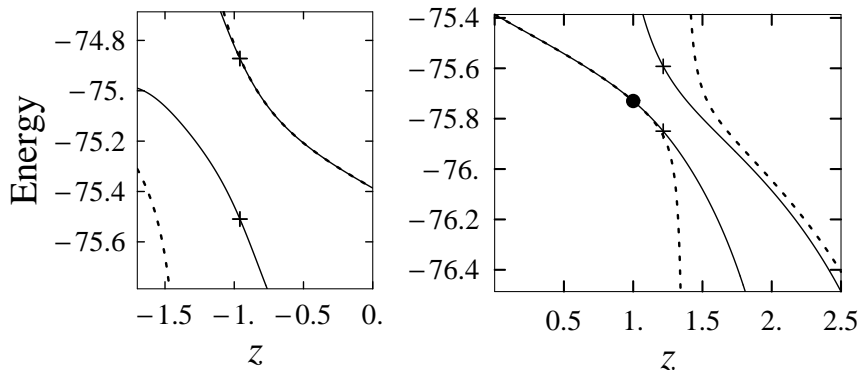


Figure 4: Energy[44] in E_h of C_2 for real z with the cc-pVDZ basis. The MP series is from Ref. [6]. Solid curves are the branches of the quadratic approximant with degrees 6, 6, and 6. Values corresponding to the real part of the branch points are marked by crosses. The dashed curve is the rational approximant with degrees 9 and 10. The filled circle shows the physical point.

5 Discussion

The MP energy function $E(z)$ is expected to have a complex-conjugate pair of square-root branch points in the positive half plane, a branch point on the negative real axis corresponding to a critical point, and, possibly, a complex-conjugate pair of square-root branch points in the negative half-plane. The complex-conjugate branch points in either half-plane result from the same physical phenomenon, avoided crossing between the ground state and a low-lying excited state. They are insensitive to changes in the basis set but shift significantly as bonds are stretched. In contrast, the critical point represents an autoionization process and its position can depend strongly on the basis.

The A/B classification scheme, based on series coefficient sign patterns, is inadequate for describing this situation. It seems more sensible to classify MP series according to singularity structure. We suggest that the complex-conjugate branch points, regardless of the real part, be referred to as “class α ” singularities while the critical point be referred to as “class β .” An atom or molecule in which the class β singularity dominates the perturbation series can be called a class β system. If the class α singularities in the positive half-plane dominate, then we have a class α system. Systems in which the positive class α singularities are approximately the same distance from the origin

as the other class α or the class β singularities can be called, respectively, class $\alpha\alpha$ or $\alpha\beta$.

Since for most applications to systems of chemical interest it is not feasible at present to compute MP series beyond 4th or 5th order, methods will have to be developed for estimating singularity positions from low-order series. For clear class α or class β systems, quadratic approximants at MP4 can give a reasonably accurate result [7]. Difficulties arise with $\alpha\alpha$ and $\alpha\beta$ systems because the approximants tend to model the multiple singularities with a single branch point half way between them [9]. One approach for dealing with this is to use a conformal mapping to shift the singular points so that one will always be somewhat closer to the origin than the other [21]. This is the basic idea behind the MP4-q λ method [8], which makes quadratic approximants in most cases a dependable tool for summing the series. In contrast, conformal mappings are less effective with partial summation, since then one must shift all singularities *away* from the origin.

An important potential application to practical quantum chemistry is to use singularity positions as a diagnostic criterion for predicting the accuracy of a calculation. This has already been implemented to some extent, using the MP4-q λ singularity positions to identify cases in which $\alpha\alpha$ and $\alpha\beta$ effects adversely affect energy accuracy. The positions of singularities in the negative half-plane seems to be an excellent diagnostic of the accuracy of the MP energy summation [8, 9]. Coupled-cluster calculations with the CCSD(T) method are relatively insensitive to the class β singularity but are affected by $\alpha\alpha$ singularity structure. The MP4-q λ singularity analysis can apparently distinguish to some extent between $\alpha\alpha$ and $\alpha\beta$ systems, and thereby serve as an accuracy diagnostic for coupled-cluster methods [10].

Another application is to multireference perturbation theory (MRPT). A key question in choosing the reference set of eigenstates is the extent of interaction between different states [45, 46, 47, 48]. Positions of the complex-conjugate branch points provide a measure of this [49]. One could monitor singularity structure along a path on the potential energy hypersurface, changing the reference set as needed to eliminate harmful branch points. At present, software is readily available only for 3rd-order MRPT [50], which is likely not sufficient for reliable singularity analysis. A 4th-order MRPT with a small reference set might benefit significantly from a quadratic approximant analysis, both for summation and for determining branch point positions.

References

- [1] C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).
- [2] D. Cremer, in *Encyclopedia of Computational Chemistry*, P. v. R. Schleyer, *et al.* eds. (Wiley, New York, 1998), pp. 1706-1735.
- [3] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978).
- [4] K. A. Petereson and T. H. Dunning, Jr., *J. Phys. Chem.* **99**, 3898 (1995); T. H. Dunning, Jr. and K. A. Peterson, *J. Chem. Phys.* **108**, 4761 (1998).
- [5] O. Christiansen, J. Olsen, P. Jørgensen, H. Koch, and P.-A. Malmqvist, *Chem. Phys. Lett.* **261**, 369 (1996); J. Olsen, O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **105**, 5082 (1996).
- [6] M. L. Leininger, W. D. Allen, H. F. Schaefer III, and C. D. Sherrill, *J. Chem. Phys.* **112**, 9213 (2000).
- [7] D. Z. Goodson, *J. Chem. Phys.* **112**, 4901 (2000).
- [8] D. Z. Goodson, *J. Chem. Phys.* **113**, 6461 (2000).
- [9] D. Z. Goodson, *Int. J. Quantum Chem.* **92**, 35 (2003).
- [10] D. Z. Goodson, *J. Chem. Phys.* **116**, 6948 (2002).
- [11] D. Z. Goodson and M. Zheng, *Chem. Phys. Lett.* **365**, 396 (2002).
- [12] C. Schmidt, M. Warken, and N. C. Handy, *Chem. Phys. Lett.* **211**, 272 (1993).
- [13] D. Cremer and Z. He, *J. Phys. Chem.* **100**, 6173 (1996).
- [14] A. Katz, *Nucl. Phys.* **29**, 353 (1962).
- [15] G. A. Baker, Jr., *Rev. Mod. Phys.* **43**, 479 (1971).
- [16] F. H. Stillinger, *J. Chem. Phys.* **112**, 9711 (2000).
- [17] J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, *Phys. Rev. A* **41**, 1247 (1990).

- [18] B. Forsberg, Z. He, Y. He, and D. Cremer, *Int. J. Quantum Chem.* **76**, 306 (2000).
- [19] D. Z. Goodson, M. López-Cabrera, D. R. Herschbach, and J. D. Morgan III, *J. Chem. Phys.* **97**, 8481 (1992).
- [20] J. Olsen, P. Jørgensen, T. Helgaker, and O. Christiansen, *J. Chem. Phys.* **112**, 9736 (2000).
- [21] C. J. Pearce, *Adv. Phys.* **27**, 89 (1978); and references therein.
- [22] D. W. Ninham, *J. Math. Phys.* **4**, 679 (1963).
- [23] C. Hunter and B. Guerrieri, *SIAM J. Appl. Math.* **39**, 248 (1980).
- [24] H. Padé, *Ann. de l'Ecole Normale Sup. 3ième Série* **9**, Suppl. 1 (1892).
- [25] G. A. Baker, Jr., and P. Graves-Morris, *Padé Approximants* (Cambridge Univ. Press, Cambridge, 1996); and references therein.
- [26] E. Brandäs and O. Goscinski, *Phys. Rev. A* **1**, 552 (1970); *Int. J. Quantum Chem.* **4**, 5718 (1970).
- [27] G. A. Baker, Jr., *The Essentials of Padé Approximants* (Academic, New York, 1975).
- [28] R. E. Shafer, *SIAM J. Math. Anal.* **11**, 447 (1975).
- [29] K. D. Jordan, *Int. J. Quantum Chem. Symp.* **9**, 325 (1975); *Chem. Phys.* **9**, 199 (1975).
- [30] V. D. Vaĭnberg, V. D. Mur, V. S. Popov, and A. V. Sergeev, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 9 (1986) [*JETP Lett.* **44**, 9 (1986)].
- [31] A. V. Sergeev, *J. Phys. A: Math. Gen.* **28**, 4157 (1995).
- [32] D. Z. Goodson and A. V. Sergeev, *J. Chem. Phys.* **110**, 8205 (1999).
- [33] P. G. Drazin and Y. Tourigny, *SIAM J. Appl. Math.* **56**, 1-18 (1996).
- [34] A. V. Sergeev and D. Z. Goodson, *J. Phys. A: Math. Gen.* **31**, 4301 (1998).

- [35] F. M. Fernández and R. H. Tipping, *J. Mol. Struct. Theochem* **488**, 157 (1999).
- [36] F. M. Fernández, and C. G. Diaz, *Eur. Phys. J. D* **15**, 41 (2001); C. G. Diaz and F. M. Fernández, *J. Mol. Struct. Theochem* **541**, 31 (2001).
- [37] M. A. H. Khan, *J. Comp. App. Math.* **149**, 457 (2002).
- [38] S. Wilson, K. Jankowski, and J. Paldus, *Int. J. Quantum Chem.* **28**, 525 (1985).
- [39] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, *J. Chem. Phys.* **103**, 4990 (1995).
- [40] Z. He and D. Cremer, *Int. J. Quantum Chem.* **59**, 15 (1996); 31 (1996); 57 (1996); 71 (1996).
- [41] W. D. Laidig, G. Fitzgerald, and R. J. Bartlett, *Chem. Phys. Lett.* **113**, 151 (1985).
- [42] P. J. Knowles, K. Somasundram, N. C. Handy, and K. Hirao, *Chem. Phys. Lett.* **113**, 8 (1985); N. C. Handy, P. J. Knowles, and K. Somasundram, *Theor. Chim. Acta* **68**, 87 (1985).
- [43] T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6769 (1992).
- [44] The plotted energy here is $E_0 + [E(z) - E_0]/z \sim (E_0 + E_1) + E_2z + E_3z^2 + \dots$.
- [45] G. Hose, *J. Chem. Phys.* **84**, 4505 (1986).
- [46] S. Zarrabian and R. J. Bartlett, *Chem. Phys. Lett.* **153**, 133 (1988); S. Zarrabian and J. Paldus, *Int. J. Quantum Chem.* **38**, 761 (1990).
- [47] J. P. Finley and K. F. Freed, *J. Chem. Phys.* **102**, 1306 (1995); and references therein.
- [48] J. Olsen and M. P. Fülscher, *Chem. Phys. Lett.* **326**, 225 (2000).
- [49] M. Warken, *J. Chem. Phys.* **103**, 5554 (1995).
- [50] H.-J. Werner, *Molec. Phys.* **89**, 645 (1996).