Advanced Review

Resummation methods

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Resummation methods can significantly improve the accuracy of *ab initio* electronic structure computations without increasing the computational cost. For perturbation theories, resummation methods can be designed by constructing approximants to model the known singularity structure of the theory in the complex plane of the perturbation parameter. Quadratic approximants for the fourth-order Møller–Plesset perturbation theory (MP4) greatly improve the accuracy for the ground-state energy and provide information about singularity positions that can be used to select an optimal summation method. The Coupled cluster theories CCSD (coupled clusters with single and double excitations), CCSDT (with triple excitations), CCSDTQ (with quadruple excitations), and CCSD(T) (with a triples correction from perturbation theory) can be resummed using approximants that model the empirically observed convergence patterns of the Hartree–Fock (HF), CCSD, CCSD(T) and HF, CCSD, CCSDT, CCSDTQ sequences. Coupling-constant perturbation theories of molecular vibration and of atoms in external fields, and semiclassical perturbation theories also benefit from appropriate approximants.

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INTRODUCTION

Perturbation theory (PT) offers a systematic technique for obtaining solutions to eigenvalue equations. In principle, it constructs a sequence of increasingly accurate approximations to the eigenvalue starting with the exact solution of a simpler equation. It would seem an obvious method for quantum chemical calculations, given that the Hartree–Fock (HF) approximation yields a qualitatively reasonable and computationally tractable approximate model. The most popular of the PTs that use the HF approximation as the starting point is the Møller–Plesset perturbation theory (MPPT),[1–4] which uses the sum of Fock operators as the zeroth-order approximation for the Hamiltonian. This theory and closely related coupled-cluster (CC) theories are the main subjects of this review.

PTs typically are formulated by introducing an expansion parameter as a measure of the strength of the perturbation. In the Schrödinger equation, $\hat{H}\Psi = E\Psi$, theHamiltonian can be written as

$$\hat{H}(z) = \hat{H}_0 + z(\hat{H}_{\text{phys}} - \hat{H}_0), \tag{1}$$

where $\hat{H}_{\text{phys}}$ is the true Hamiltonian, z is the perturbation parameter, and $\hat{H}_0\Psi_0 = E_0\Psi_0$ is a computationally tractable initial approximation. By construction, the true Schrödinger equation corresponds to $z = 1$. The PT algorithm[2] gives a solution in the form of an infinite power series,

$$E \sim \sum_{j=0}^{\infty} E_j z^j. \tag{2}$$

It is rarely possible in practice to calculate an infinite number of terms. Usually, one must truncate the series at some finite-order n,

$$E \sim \sum_{j=0}^{n} E_j z^j. \tag{3}$$

In the case of MPPT, $n = 4$ is typically the highest order computationally tractable. The series can be computed to higher orders for small molecules, and these provide important benchmarks for theoretical understanding.

Note that Eq. (3) is a polynomial. Finite-order PT yields a polynomial approximation for

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the eigenvalue. The true function $E(z)$ has a much more complicated functional form than a polynomial. 'Resummation' consists transforming Eq. (3) into a new functional form that more closely resembles the true $E(z)$. This can give a significantly more accurate estimate for the physical E at virtually no additional computational cost.

We begin with a review of relevant background from complex analysis. The central idea is that failure of the polynomial approximation is due to singularities in $E(z)$ at particular values of z in the complex plane. The singularity structure of $E(z)$ for MPPT can, to some extent, be predicted in advance from general principles. This is the topic of the section *Singularity Structure of Møller–Plesset Perturbation Theory*. *Modeling the Singularities* describes the use of approximants to model the singularity structure while *Moving the Singularities* describes the use of conformal mappings to shift the positions of singularities in order to mitigate their effect. A mixed approach that uses an approximant and a conformal mapping provides a useful technique for improving fourth-order MPPT. As an added benefit, it gives estimates of singularity positions that inform the selection of an appropriate computational method. The section *Coupled-Cluster Theories* considers CC theories and *Other Applications* gives a brief overview of resummation methods for other kinds of perturbation theories. *Conclusions* presents a recommended strategy for choosing an appropriate method for an electronic structure computation.

MATHEMATICAL BACKGROUND

Let $\hat{H}_0$ be the zeroth-order approximation for the Hamiltonian operator $\hat{H}$. The zeroth-order energy E_0 is then the sum of filled electron orbital energies. The 'Hartree–Fock approximation' for the energy is $E \approx E_0 + E_1$, corresponding to the first-order perturbation series evaluated at $z = 1$. The second-order approximation $E_0 + E_1 + E_2$ is called MP2 and, in general, $\sum_{j=0}^{n} E_j$ is called MPn.

Because the physical solution corresponds to $z = 1$, the perturbation parameter is usually not explicitly included in the analysis. However, to understand MPn convergence, it is important to keep in mind that what we are doing is expanding a function in a Taylor series about $z = 0$ and then evaluating the series at $z = 1$. The Taylor series, expressed as a polynomial in z, can be used to construct a function $E(z)$ where z is a free variable in the complex plane.

The modern theory of functions of a complex variable is largely based on the idea of building up a function from its singular points. A *singular point* (also called a *singularity*) is a point where the function or its derivative becomes infinite or undefined, or where the function becomes multiple valued. The kinds of singular points relevant to the present discussion are *poles* and *branch points*. A point z_s is a pole if the singular behavior can be removed by multiplying the function by $(z - z_s)^m$, where m is a positive integer and $\lim_{z \to z_s} (z - z_s)^m f(z)$ is nonzero. The value of m is called the *order* of the pole. A branch point is a point at which the function becomes multiple valued. For example, $f(z) = (z - 1)^{1/2}$ has two branches: the positive branch, on which $4^{1/2} = +2$, and the negative branch, on which $4^{1/2} = -2$. If one continues $f(z) = (z - 1)^{1/2}$ on the positive branch from $z = 5$ for decreasing real z, the function remains well defined, and single valued, until the branch point at $z = 1$ is reached, where the positive and negative branches give the same value, $f = 0$. Continuing on a closed path in the complex plane around a branch point causes a transition from one branch to another. For example, continuing along the circular path $z = 5e^{i\theta}$ for θ from 0 to 2π, we transform f on the positive branch from $(5e^0 - 1)^{1/2} = 2$ to

$$\begin{aligned}(5e^{2\pi i} - 1)^{1/2} &= e^{\pi i}(5 - e^{-2\pi i})^{1/2} \\ &= (-1)(5 - 1)^{1/2} \\ &= -2.\end{aligned}$$

The central importance of singular points in the theory of infinite series comes from the following theorem:

Theorem 1. *The Taylor series about a point z_0 of a function over the complex z plane will converge at a value z_1 if the function is nonsingular at all values of z in the circular region centered at z_0 with radius $|z_1 - z_0|$. If the function has a singular point z_s such that $|z_s - z_0| < |z_1 - z_0|$, then the series will diverge when evaluated at z_1.*

The radius of the circle defined by all z such that $|z_0 - z| = |z_0 - z_s|$ is called the *radius of convergence* of the series. A function within its circle of convergence is said to be *analytic*. A function that is analytic at all noninfinite points in the complex plane is said to be *entire*. In particular, a polynomial of finite order, such as Eq. (3), is an entire function. Therein lies the difficulty with MPPT. The true function $E(z)$ has a rich singularity structure (described in the next section). The MP series tries to model this with a function that is nonsingular.

The following related theorem was proved by Darboux[5,6]:

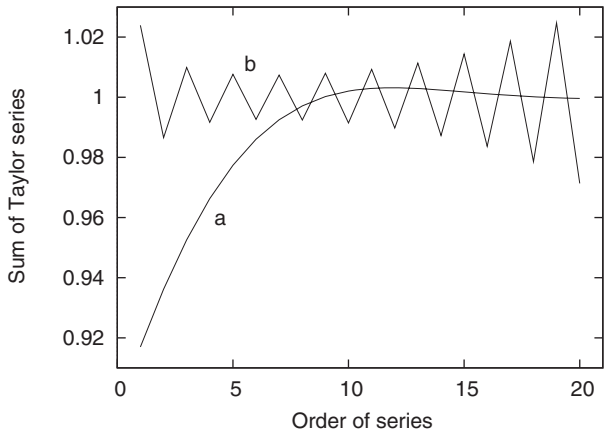

FIGURE 1 | Typical convergence patterns for Møller–Plesset perturbation theory, given by the model functions f_a and f_b of Eq. (4).

Theorem 2. *In the limit of large order, the series coefficients become equivalent to the Taylor series coefficients of the singularity closest to the origin.*

These theorems are important but they are not the whole story. The convergence or divergence they predict is guaranteed to happen eventually, in the limit of large order, but at low orders a divergent series might seem to converge quite well. Indeed, there are many examples of MP series that diverge at large order but for which fourth-order PT (MP4) gives a very accurate ground-state energy. There are also molecules for which the series is convergent, but only at a very slow rate, so that MP4 is not very accurate.[7–15]

Consider the following two functions:

$$f_a(z) = 0.850 + (0.425) \times \sqrt{(1.05 + 0.35i - z)(1.05 - 0.35i - z)}, \quad (4a)$$

$$f_b(z) = 0.713 + (0.214)\sqrt{z + 0.8}. \quad (4b)$$

At $z = 1$, we have $f_a(1) = f_b(1) = 1.00$. The Taylor series of f_a about $z = 0$ is convergent at $z = 1$, with radius of convergence 1.107, while the Taylor series of f_b is divergent, with radius of convergence 0.8. Nevertheless, at low orders the series for f_a is less accurate than the series for f_b. The convergence behaviors of these two series are compared in Figure 1. The very slow convergence for f_a is due to the fact that the singular points are close to the point of summation, $z = 1$. Some of the more intractable MP series have a complex–conjugate pair of singularities just beyond the physical point $z = 1$. This happens when there is a low-lying excited state with the same symmetry as the ground state.

When the HF solution is used as the zeroth-order approximation, the theory is formulated within a finite-dimension Hilbert space. The operators $\hat{H}_0$ and $\hat{H}_1$ can then be expressed as matrices $\mathbf{H}_0$, $\mathbf{H}_1$. The following theorem describes the solutions of a matrix eigenvalue equation:

Theorem 3. *The eigenvalues E of an $n \times n$ matrix* $\mathbf{H}$ *are the roots of the polynomial*

$$p(E) = \det(\mathbf{H} - E\mathbf{I}),$$

where $\mathbf{I}$ *is the $n \times n$ identity matrix.*

Here, 'det' is the matrix determinant; $p(E)$ is called the *characteristic polynomial*.

SINGULARITY STRUCTURE OF MØLLER–PLESSET PERTURBATION THEORY

Square-Root Branch Points

Consider a 2×2 matrix eigenvalue equation

$$(\mathbf{H}_0 + z\mathbf{H}_1)\mathbf{v} = E\mathbf{v},$$
$$\mathbf{H}_0 = \begin{pmatrix} a_0 & 0 \\ 0 & b_0 \end{pmatrix},$$
$$\mathbf{H}_1 = \begin{pmatrix} a_1 & c \\ c & b_1 \end{pmatrix}, \quad (5)$$

where $\mathbf{v}$ is a two-dimensional column vector and the unperturbed eigenvalues are given in increasing order, i.e., $a_0 < b_0$. The solutions for the eigenvalues are the roots of the characteristic polynomial

$$p(E) = (a_0 + za_1 - E)(b_0 + zb_1 - E) - z^2c^2. \quad (6)$$

Solving $p(E) = 0$ for E gives the two solutions:

$$E(z) = \frac{1}{2}[a + b \pm \sqrt{(b-a)^2 + 4z^2c^2}],$$
$$a = a_0 + za_1,$$
$$b = b_0 + zb_1. \quad (7)$$

For any z on the real axis, $E(z)$ is nonsingular. However, there exist two complex values of z at which the argument of the square root goes to zero and the two branches cross,

$$z = \frac{b_0 - a_0}{b_1 - a_1 \pm 2ci}. \quad (8)$$

These are branch-point singularities of $E(z)$.

The nth degree characteristic polynomial of the $n \times n$ matrix eigenvalue problem was analyzed by Katz,[16–18,a,b] who proved the following:

Theorem 4. *Consider an $n \times n$ matrix eigenvalue problem* $\mathbf{H}(z)\mathbf{v} = E\mathbf{v}$ *in which* $\mathbf{H}$ *is an Hermitian*

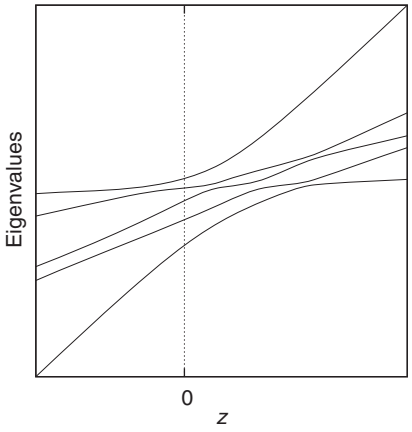

FIGURE 2 | Avoided crossings in a 5 × 5 matrix eigenvalue perturbation theory as a function of the perturbation parameter z along the real axis.

matrix and the elements of **H** *are entire functions of z. Assume that no two eigenvalues are equal at any real value of z. Let* $E_0(z)$, $E_1(z)$, $E_2(z)$, . . ., $E_n(z)$ *be the eigenvalues of a given symmetry (e.g., with the same angular momentum quantum numbers) in order of increasing value. Then for each pair* $E_j(z)$, $E_k(z)$ *there exists a complex–conjugate pair of branch points* z_{jk}, z^*_{jk}, *with nonzero imaginary parts, that connect the functions* $E_j(z)$ *and* $E_k(z)$. *In the neighborhood of* z_{jk} *the functions behave as*

$$E_{jk} \pm \gamma_{jk}\sqrt{z - z_{jk}},$$

with $E_{jk} = E_j(z_{jk}) = E_k(z_{jk})$ *and*

$$\gamma_{jk} = 2\left(\frac{\partial p}{\partial z} \Big/ \frac{d^2 p}{dE^2}\right)\Bigg|_{z=z_{jk}, E=E_{jk}}, \qquad (9)$$

where $p(E(z))$ *is the characteristic polynomial.*

Thus, each branch $E_j(z)$ of the energy function will have n complex–conjugate pairs of square-root branch points somewhere in the complex plane off the real axis. If one plots the eigenvalues over a domain of real z they exhibit avoided crossings, avoided because there are no branch points on the real axis. This is illustrated by Figure 2, for a 5 × 5 matrix. The real z value of closest approach between E_j and E_k corresponds approximately to the real part of z_{jk}. The smaller the imaginary part of z_{jk}, the sharper the crossing.

Critical Point Singularities

Another kind of singularity, for MPPT, was predicted by Stillinger.[19] Suppose z in Eq. (1) is a negative real number. zH_{phys} contains interelectron potential energy as

$$z\sum_{j<k} r_{jk}^{-1}.$$

If z is negative, electrons no longer repel each other—they attract each other. The operator $\hat{H}_0$ contains the repulsive mean-field potential energy, a static potential field distributed according to the ground-state HF orbitals. Because it is multiplied by $(1 - z)$, this destabilizing potential becomes stronger as z is made increasingly negative. If the magnitude of the negative z becomes sufficiently large, the system will ionize and, in principle, rearrange itself into a bound electron cluster dissociated from the nuclei.

A z value where binding undergoes a sudden qualitative change is analogous to a critical point in thermodynamics. This had been studied earlier by Baker[20] in the context of nuclear structure PT and is a general phenomenon in the quantum mechanics many-fermion systems.[21] At the critical value of z, $E(z)$ switches to a different branch. It will have a branch point somewhere on the negative real-z axis at which the two branches have the same energy. Baker showed that this is formally equivalent to a critical point in the energy as a function of the volume of the system.[c] The perturbation parameter plays the role of temperature.

Does this contradict Katz's theorem, which claims that all the singular points have nonzero imaginary part? No, it does not—the Baker–Stillinger analysis holds for the full infinite-dimension Hilbert space but not for the finite-dimensional spaces used in practice. The perturbation series is asymptotically equal not to the true ground-state energy eigenvalue but rather to the exact solution for the lowest eigenvalue of the finite-dimension Hamiltonian matrix. This matrix eigenvalue is called the *full configuration interaction* (FCI) approximation to the true energy.

Nevertheless, given a large enough finite-dimension basis set, $E(z)$ will presumably show singular behavior close to the real axis in the neighborhood of the critical point. This was addressed by Sergeev and coworkers[22,23] with FCI computations as a function of z for a variety of atoms and small molecules. They used various of the correlation-consistent basis sets and found that the behavior of the eigenvalue spectrum at negative z depended strongly on which basis was used. For Ne with a compact basis set (cc-pVDZ),[24] no critical point was seen. If the basis was augmented with diffuse functions (aug-cc-pVDZ),[25] a sharp avoided crossing was seen at which many states almost crossed near a particular negative real z. For z beyond the critical point, the ground state was a fully ionized Ne^{8+} (due to the frozen-core

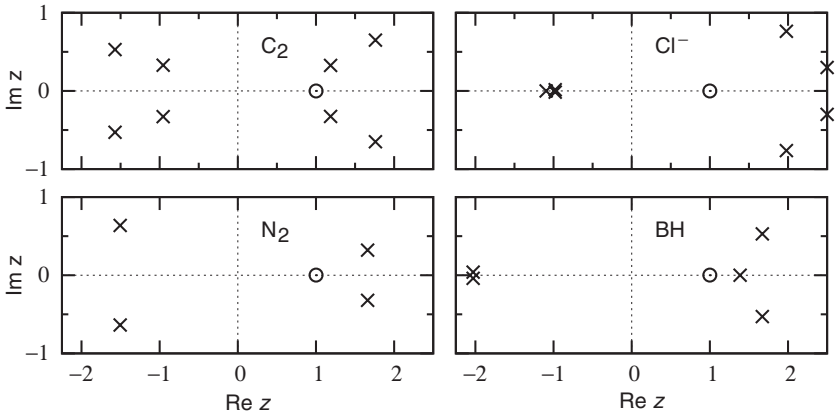

FIGURE 3 | Branch points locations of the ground-state Møller–Plesset energy function[23] for the C_2 molecule (cc-pVDZ basis), the chloride ion (aug-cc-pVDZ), the N_2 molecule (cc-pVDZ), and the boron hydride molecule (aug-cc-pVQZ). C_2 and N_2 are of class $\alpha|\alpha$, Cl^- is of class-$\beta|\alpha$, and BH has a complicated singularity structure, technically of class $\beta|\beta$ but best described as x$|\alpha$. The circle marks the physical point, $z = 1$.

approximation only valence electrons are affected) and, in contrast to Stillinger's prediction, there was no electron cluster but rather 8 free electrons. This was because the basis functions, all centered at the nucleus, were unable to model a dissociated electron cluster. By analyzing the large-order MP series, which were extracted from the FCI computations, they identified (using approximants, as described in the next section) clusters of Katz branch points very close to the negative real axis.

They found that the hydrogen fluoride molecule had a critical point even with a compact basis set. Basis functions centered on the H atom were able to model a bound cluster of the fluorine valence electrons, giving in effect a H^{7-} anion and a F^{7+} cation separated by the $z = 1$ equilibrium bond distance (which was held fixed for the computation). With the cc-pVDZ basis, the critical point was far from the origin, at -1.28. With the aug-cc-pVDZ, it moved in to -0.76.

There is yet another kind of singularity one can find in $E(z)$. Consider the effect of increasing z along the real axis past $z = 1$. The mean-field potential becomes attractive but electron correlation becomes more strongly repulsive. Sergeev and coworkers[22,23] found that for some systems, such as Ar with aug-cc-pVDZ, the latter effect prevailed resulting in a critical point at positive real z corresponding to one-electron ionization. For most of the other systems that they studied, the singularities in the positive half-plane consisted only of isolated branch points off the real axis.

Classification Schemes for MP Series

Various classification schemes have been proposed for characterizing MP series. Schmidt et al.[27] classified series according to the sign patterns of the E_j: Those for which E_3 and E_4 have the same sign were put in 'class A' while those for which E_3 and E_4 have different signs were put in 'class B'. Cremer and coworkers[10,28–31] identified these sign patterns with qualitative physical characteristics of the electronic structure. They noted that molecules for which the valence electron distribution is spacious, such as BH and CH_2, have monotonic but slow class-A convergence. In contrast, for molecules with a crowded electron distribution, typically due to the presence of highly electronegative atoms, the series coefficients beyond the lowest orders alternate in sign but give a relatively more accurate value for the energy. Cremer and coworkers[28,31] proposed that the spacious electronic structure be called 'type I' and the crowded structure, 'type II'. They noted that the series behavior for type II systems varies considerably depending on the nature of the basis set.

An alternative is to classify systems according to singularity structure.[23,32] Let us describe an isolated complex–conjugate pair of square-root branch points as a 'class-α' singularity and a critical point on the real axis as a 'class-β' singularity, and let us refer to the closest singularity to the origin in either half-plane as the dominant singularity in that half-plane. As was shown in Figure 1, slow monotonic convergence is consistent with class α in the positive half-plane while alternating signs are consistent with class β at negative z.

We will see that the choice of resummation strategy depends on the nature of the dominant singularity in each half-plane. One can classify systems as $\beta|\alpha$ if the dominant singularity in the negative half-plane is of class β and that in the positive half-plane is of class α, as class $\alpha|\alpha$ if both dominant singularities are of class α, and so on. Examples are shown in Figure 3. This classification scheme allows for more subtle distinctions. A system such as boron hydride is technically of class $\beta|\beta$. However, the dominant singularity in the negative half-plane is so distant from

the origin as to be insignificant, while there is a class-α singularity that is almost as close to the origin as the class-β singularity in the positive half-plane. This can be described as class x|$\beta\alpha$, or simply as x|α, because in general a class-α singularity has stronger effect on series behavior than does a class-β singularity at the same radius. The magnitude of the contribution of a singularity to the series coefficients depends on two characteristics: the distance from the origin and the magnitude of the prefactor that multiplies the square-roots. At high order only the distance from the origin is relevant—the closer to the origin, the more quickly the singular term dominates the series coefficients. At low orders the magnitude of the prefactor is relevant. Singularities of class β have much smaller prefactors than do those of class α. Another example is the Ne atom with a compact basis set. It is technically in class $\alpha|\alpha$, but both dominant singularities are very far from the origin, and the conventional sum of the MP series converges rapidly. This can be described as class x|x.

The effect of the choice of basis on type-II systems can be explained in terms of singularity analysis. A correct description for type II in the limit of large basis set has a dominant class-β critical point at negative z. For an atom, a compact basis lacks the flexibility to model the dissociation at the critical point, and thus in effect converts a system such as Ne or F^- into type I. N_2, with a crowded triple bond, in principle ought to be of type II, but with the cc-pVDZ basis it behaves as type I with class-$\alpha|\alpha$ singularity structure,[33] as is evident in Figure 3.

These classifications based on the electronic orbital structure and singularity structure are more fundamental and therefore preferable to the older class A/B scheme. In fact, the variety of series coefficient patterns generated by different combinations of singularities is such that at least five different classes would be needed for a full description in terms of sign patterns.[31]

MODELING THE SINGULARITIES

The nth partial sum is

$$s_n(z) = \sum_{j=0}^{n} E_j z^j. \tag{10}$$

It is typical in the literature to report $E_0 + E_1$, the HF energy, rather than the individual values E_0 and E_1. It is convenient, then, to write the partial sum as

$$S_n = \sum_{j=0}^{n} \epsilon_j z^j, \quad \epsilon_0 = E_0 + E_1, \quad \epsilon_{j>0} = E_{j+1}; \tag{11}$$

i.e., $S_n = E_0 + z^{-1}(s_{n+1} - E_0)$. Note that MP3 corresponds to S_2, MP4 to S_3, and so on. At the physical point $z = 1$, S_n and s_{n+1} are equal. In practice, it makes little difference whether one applies resummation methods to S_n or to s_{n+1}, because the values of the coefficients E_0 and E_1 are mostly determined by nonsingular contributions from $E(z)$.

Seeing as the convergence difficulties come from trying to model a function $E(z)$ with prominent singularities using a polynomial $S_n(z)$ that has no singularities, an obvious strategy is to replace $S_n(z)$ with a functional form that is not entire. We will need a criterion for parameterizing the new functional form. A useful strategy is to require that the nth-order Taylor series of the new functional form be equivalent to S_n. In other words, the coefficient that multiplies z^j in the Taylor series of the new functional form must equal ϵ_j. Because the Taylor series of a function is unique, this gives a set of equations sufficient to determine $n+1$ parameter values. The resulting function is called an *approximant*.

This approach was developed by Padé in his 1892 doctoral thesis.[34] His name is usually associated with rational approximants,

$$S_{[M/N]}(z) = P(z)/Q(z), \tag{12}$$

where P and Q are polynomials of degrees M and N, respectively, and $Q(0) = 1$. Linear equations that determine the coefficients of the polynomials are obtained by collecting terms according to power of z in the equation $QE \sim P$, where E here represents the power series for $E(z)$. Rational approximants contain poles at roots of Q, which is not consistent with the singularity structure of a matrix eigenvalue PT.

A less familiar form of approximant is the *quadratic approximant*,[35,36] composed of three polynomials, $P(z)$, $Q(z)$, and $R(z)$, of degrees L, M, and N, with $Q(0) = 1$. The coefficients of the polynomials are determined by the linear equations obtained from:

$$QE^2 - PE + R \sim 0. \tag{13}$$

The (A closely related technique is to solve for the roots of an effective characteristic polynomial.[37]) approximant resulting from Eq. (13) is

$$S_{[L/M,N]}(z) = \frac{1}{2Q(z)} \times \left(P(z) \pm \sqrt{P(z)^2 - 4Q(z)R(z)}\right). \tag{14}$$

Given a perturbation series of order n, the degrees of the polynomials must be chosen such that

$$L + M + N = n - 1. \tag{15}$$

Equation (14) has square-root branch points, at roots of the discriminant polynomial

$$D(z) = P^2 - 4QR. \tag{16}$$

This advantage of quadratic approximants was noted by Vaĭnberg et al.[38] in a study of the PT for an atom in an electric field in powers of the field strength. The bound state of the atom is then only metastable. The ground-state eigenvalue is complex, with the lifetime of the state determined by the imaginary part. Quadratic approximants put a branch point on the positive real axis, giving a complex energy in reasonable agreement with the exact result. Quadratic approximants had earlier been used by Jordan[39,40] to extrapolate diatomic potential energy curves into regions affected by an avoided crossing. Quadratic approximants give convergent results[14] for even the most divergent of the MP series of Olsen and coworkers[11,12] and Leininger et al.[13]

However, the singularity structure of Eq. (14) is not quite identical to that required by Katz's theorem. $S_{[L/M,N]}(z)$ has just two branches, corresponding to the plus or minus sign. In fact, the ground-state energy function $E(z)$ has n different branches, one for each eigenvalue in the n-dimensional Hilbert space. Padé noted that approximants could be constructed from a polynomial in E of any degree. The number of branches in the approximant equals the degree of the polynomial. Approximants with multiple branches can also be constructed from differential equations ('Hermite–Padé approximants').[41] In practice, more complicated approximants perform no better than quadratic approximants unless the perturbation series is known to very high order.[42,43] At the moderate orders available from MPPT, quadratic approximants give a reasonable description of the ground-state branch in the neighborhoods of its branch points, mimicking the local functional form required by Katz's theorem.

Quadratic approximants give convergent results for singularity positions.[23] The convergence is quickest for singularities closest to the origin of the z plane, but with increasing series order the positions gradually converge for more and more distant singularities. This allows one to extract estimates of the branch point positions using high-order MP series extracted from benchmark FCI computations.[8,9,11–13,15] This is usually more convenient than searching for avoided crossings[22] or solving directly for crossing points in the complex plane.[26]

Although the quadratic approximants converge dependably at large order, their success for directly summing MP4 is mixed.[14] Consider the approximant with index [1/0,1]. It has two branch points,

$$z_1 = \left(\frac{\beta}{\alpha} + 2\gamma\right)^{-1}, \quad z_2 = \left(\frac{\beta}{\alpha} - 2\gamma\right)^{-1}, \tag{17}$$

where

$$\alpha = \epsilon_2/\epsilon_1, \quad \beta = \epsilon_3/\epsilon_1, \quad \gamma = (\beta - \alpha^2)^{1/2}. \tag{18}$$

In practice, we usually have $\beta > \alpha^2$, which means that z_1 and z_2 are pure real. This approximant performs poorly when $E(z)$ has singularities in both the positive half-plane and in the negative half-plane roughly equidistant from the origin. The approximant is unable to simultaneously model both singular regions. Instead, it tends to put its branch points approximately half-way between, close to the origin.[33,44] This problem is remedied by the MP4qλ resummmation method,[44] described in the next section.

Rational Padé approximants, the traditional 'Padé approximants', are also able to sum MP series.[10,14,15,45] They are less reliable than the quadratic approximants for MP4, but at high order they converge to the FCI result about as well as quadratic approximants, even though the only singularities in the approximants are poles. They accomplish this by mapping out branch cuts with nearly coincident poles and zeros.[46,47] However, quadratic approximants have the advantage at high order of giving reliable estimates of the branch point locations as well as an estimate of the energy.[14,23]

Another approach to determining singularity positions is to take advantage of Darboux's theorem, Theorem 2. The D'Alembert ratio test, which gives the radius of convergence of the partial sums as $|\epsilon_j/\epsilon_{j+1}|$ in the limit of large j, is a well-known example of a Darboux-type method, but other more sophisticated techniques are available.[5,6,48–51] The advantage of these is that Darboux's theorem provides a degree of mathematical rigor that approximant methods lack. The disadvantage is that for low-order series, approximants tend to work better in practice than do Darboux methods.

MOVING THE SINGULARITIES

Only two points in the complex z plane have a fixed meaning: $z = 0$ represents the zeroth-order approximation while $z = 1$ represents the true solution. We are free to redefine all other points with an arbitrary mapping. In particular, we can choose a mapping that avoids the situation of branch points approximately equidistant from the origin.

Consider a bilinear conformal mapping,[52]

$$u = \frac{z}{1 - \lambda + \lambda z}. \tag{19}$$

The complex plane of coordinate z is mapped to the complex plane of a new coordinate u. The mapping is characterized by the free parameter λ. Note, however, that 0 is always mapped to 0 and 1 is always mapped to 1. The inverse mapping is

$$z = \frac{(1-\lambda)u}{1 - \lambda u}. \tag{20}$$

Equation (20) can be expanded in a Taylor series in u, substituted into the original series, and then the terms can be collected according to powers of u. The resulting coefficients of the u series are

$$\tilde{\epsilon}_k(\lambda) = \sum_{j=1}^{k} \binom{k-1}{j-1} \lambda^{k-j}(1-\lambda)^j \epsilon_j, \tag{21}$$

in terms of binomial coefficient $\binom{k-1}{j-1}$.

Because 0 and 1 are fixed points, the new series evaluated at $u = 1$ still corresponds to the physical solution and $u = 0$ still corresponds to the zeroth-order approximation. All other points in the complex plane are shifted. For real λ ranging from $-\infty$ to ∞ any given point in the complex plane moves along the circle that passes through the two fixed points and the original ($\lambda = 0$) location of the point in the z plane, as shown in Figure 4. Pure real points (other than 0 and 1) are shifted along the real axis.

This mapping has a long history in quantum chemical PT but under different guises. Schmidt et al.[27] found that Eq. (21) can be obtained by introducing scaling factors into the Hamiltonian, according to a procedure developed by Feenberg.[53] The Feenberg scaling is itself a special case of a more general scaling method developed by Dietz and coworkers,[54–56] in which the scaling factor is an operator $\hat{\Lambda}$ rather than just a constant λ. Szabados[57] has shown that the Feenberg scaling is closely related to an empirical scaling procedure that Grimme developed[58] for improving the accuracy of MP2.

The choice of λ is in principle arbitrary. Goldhammer and Feenberg[61] proposed choosing λ so as to minimize the correlation energy,

$$E_{\text{corr}} = E - E_{\text{HF}} \approx \sum_{k=2}^{n} \tilde{\epsilon}_{k-1}(\lambda), \tag{22}$$

with the series truncated at specified order n. This is not justified by any rigorous variational theorem but it can convert divergent MP partial sums into convergent sums at high order and can often improve the accuracy of MP4 partial sums. Amos[59] noted that the Goldhammer–Feenberg criterion is equivalent to assuming that the high-order terms behave as a geometric series.[60] Forsberg et al.[31] showed that it is equivalent to forcing $\tilde{\epsilon}_{n-1}$, the highest-order coefficient before truncation, to be zero. This ensures that the truncated series will qualify as an 'optimal asymptotic approximation' (as defined by Bender and Orszag[62]) at order $n - 2$. In practice,[31] the Goldhammer–Feenberg criterion reliably improves the convergence of the partial sum, S_n, for the many systems in which a class-β singularity on the negative real axis dominates the behavior of the perturbation series. It does this by shifting the dominant singularity, on the negative real axis, away from the origin.[14]

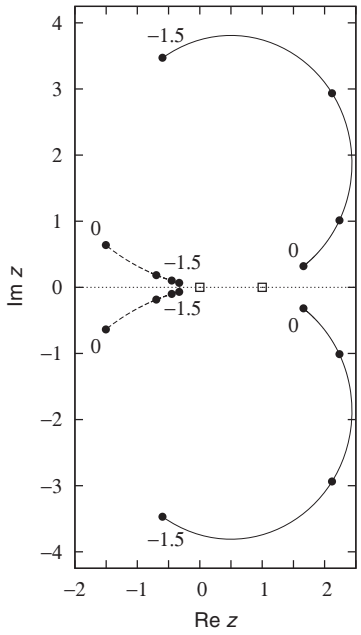

FIGURE 4 | Effect of the bilinear mapping on a class $\alpha|\alpha$ system. The mapping parameter λ ranges from 0 to −1.5 as indicated in increments of −0.5. The squares show $z = 0$ and 1, the fixed points of the mapping.

However, the Goldhammer–Feenberg criterion is not optimal for use with quadratic approximants, because then the goal is not to increase the radius of convergence but rather to modify the singularity structure so that it can be modeled by the approximant. In particular, one needs to avoid the situation with singularity structure in both half-planes approximately equidistant from the origin. The MP4qλ resummation method[44] uses a quadratic approximant to sum the series in u with λ chosen such that the position of the singularity of the approximant in a given half-plane is shifted as far as possible from the origin. Using the [1/0,1] approximant, the optimal λ values

are[33]

$$\lambda_{p,n} = \frac{1}{\alpha - 1}\left[\frac{\gamma}{\gamma \pm (\alpha - 1)} + \alpha\right], \qquad (23)$$

with α and γ from Eq. (18). Here λ_p, the value that maximizes the branch point position in the positive half of the u plane, is given by the '+' solution, whereas the '−' gives λ_n, which maximizes the position in the negative half of the u plane. The resulting branch point positions in the z plane, after the inverse mapping of Eq. (20), are

$$z_{p,n} = \left(\alpha + \frac{2\gamma^2}{\alpha - 1} \pm 3\gamma\right)^{-1}. \qquad (24)$$

For dominant class-α branch points, Eqs (24) give reliable estimates for the real part of the singularity positions.[33] Class-β singularities, however, are not isolated branch points, and therefore are modeled less accurately by quadratic approximants. Class-β singularity structure consists of clusters of branch points with very small prefactors.[23] Approximant [1/0,1] models this using an isolated branch point with a larger prefactor but farther from the origin. The qλ approximant then exaggerates the effect of the conformal mapping and ends up with the singularity too close to the origin. It is interesting that the average of these two inaccurate estimates gives a remarkably reliable estimate of the class-β singularity position.[33]

Evaluating the [1/0,1] approximant at λ_p is a reasonably good method for summing MP4 for type-I systems, in which the most important singularity structure, typically of class α, is found in the positive half-plane. For type-II systems this approximant is not appropriate. In the limit $z \to 0$, the discriminant goes to zero and the two branches have the same energy. This is a qualitatively reasonable zeroth-order approximation for a type-I system, in which the singularity corresponds to a crossing of two states that are close in energy within the HF approximation as well as in the exact solution. However, a type-II system typically has a class-β critical point, which corresponds to a crossing of the ground state with a state that has a very high HF energy.[22] This can be modeled using a [1/0,2] approximant with an extra parameter that is chosen by constraining the approximant to have the desired qualitative behavior.[14] The choice $r_0 = 0$ gives the HF energy for the lower branch at $z = 0$ and zero energy for the upper branch. This approximant has branch points at

$$u_1 = [\tilde{\epsilon}_3(\lambda)/\tilde{\epsilon}_2(\lambda) + \sqrt{-4\tilde{\epsilon}_2(\lambda)/\epsilon_0}]^{-1},$$
$$u_2 = [\tilde{\epsilon}_3(\lambda)/\tilde{\epsilon}_2(\lambda) - \sqrt{-4\tilde{\epsilon}_2(\lambda)/\epsilon_0}]^{-1}. \qquad (25)$$

The extrema as a function of λ can be solved for numerically. At negative λ the extrema are typically on the negative real axis, with the one closest to the origin given by u_2. Let us call this dominant singular point u_n. Evaluating the [1/0,2] approximant at u_n gives the 'constrained' MP4qλ method, which in practice usually gives a better result than does MP4qλ [1/0,1] for type II.[44,63]

Because singularity structure for type-II systems is being modeled less accurately than for type I, which really has isolated branch points, the resummation accuracy for type II is better when the singularity can be shifted relatively farther from the origin. The maximum distance $|z_n|$ to which the dominant singularity of the constrained approximant on the negative real axis can be shifted is strongly correlated with resummation accuracy and can serve as a diagnostic. For a benchmark set of type-II systems, the number of accurate digits in the correlation energy was found[64] to follow the linear relation $0.3 + 1.1|z_n|$.

Despite significant improvement to MP4 from resummation, there are many systems for which the accuracy is still rather poor, due to the presence of a class-α singularity rather close to $z = 1$ along with singularity structure of either class in the negative half-plane with real part significantly closer to the origin than -1. The MP4 series does not contain enough information to simultaneously model all these singularities, and the proximity to the fixed points $z = 0$ and $z = 1$ makes it difficult to mitigate their effects by shifting the positions. This problem becomes especially severe in the description of homolytic bond cleavage when using a spin-restricted HF zeroth-order approximation, which has an incorrect dissociation limit. As the bond is stretched, the energy spacing between the ground state and the first excited state of the same symmetry decreases, resulting in intractable branch points close to the fixed points. This causes the accuracy of the resummation to depend rather strongly on bond distance.[65] CC theories, described in next section, seem to be less sensitive to this effect.

The resummation methods described here are size extensive as long as the underlying theory (e.g., MPPT) is size extensive. They are not exactly size consistent for dissociation into nonidentical fragments.[57,64,66] However, they are qualitatively size consistent[64] and the small size inconsistency seems to rapidly decrease with increasing basis size.[66] The size inconsistency results from the dependence of the optimally shifted singularity positions on molecular geometry. The resummation can be made exactly size consistent by choosing a single fixed value for the mapping parameter λ instead of optimizing λ at each nuclear configuration.[57,67]

Computer algorithms are available for directly computing MP5[68,69] and MP6.[70,71] Concern over the potential divergence of higher-order series has perhaps scared people away from these, and led them to use more expensive CC methods instead. However, MP5 and MP6 even without resummation seem to give dependable results for molecular energies at equilibrium geometries,[72] and the accuracy can be improved with a higher-order version of the Goldhammer–Feenberg transformation[27,28,31,73] or with quadratic approximants.[14] In principle, resummation strategies based on singularity shifting could also be used for higher-order MP series, but this has yet to be studied systematically. The singularity structure of higher-order quadratic approximants is rather complicated and there are many more ways to formulate the approximants than at fourth order.

COUPLED-CLUSTER THEORIES

CC theory is a popular alternative *ab initio* method for improving an initial HF approximation. In fact, it is closely related to MPPT.[3,4,15,74] The basic idea is to express the wavefunction in the form

$$\Psi = e^{\hat{T}}|0\rangle. \tag{26}$$

$|0\rangle$ is a zeroth-order ground state (typically the HF approximation) and $\hat{T}$ is an operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots, \tag{27}$$

where $\hat{T}_j$ is proportional to the creation operator $a_j^\dagger$ that transforms $|0\rangle$ into $|j\rangle$. The exponential of an operator is defined in the form of a Taylor series,

$$e^{\hat{T}} = 1 + \sum_{m=1}^{\infty} \frac{1}{m!}\hat{T}^m, \tag{28}$$

where $\hat{T}^m$ represents operating m times with $\hat{T}$. Substituting Eqs (28) and (27) into Eq. (26), we obtain the FCI linear combination with coefficients to be determined from the Schrödinger equation.

If we use the z-dependent form of the Hamiltonian, Eq. (1), then the creation operators consist of operators proportional to powers of z. Collecting the terms in the Schrödinger equation according to power of z and ignoring degrees greater than n, one obtains algebraic equations that can be solved analytically for the wavefunction coefficients. This yields the MPn series. On the other hand, if one instead truncates the expansion for $\hat{T}$, Eq. (27), throwing out all terms beyond some specified $\hat{T}_m$, then one obtains a set of nonlinear equations for the wavefunction coefficients that can be solved iteratively for a numerical solution. Truncating after $\hat{T}_2$ gives the CCSD method, truncating after $\hat{T}_3$ gives the CCSDT method, and truncating after $\hat{T}_4$ gives the CCSDTQ method.

According to Eq. (28), $e^{\hat{T}}$ is the exact sum of an infinite number of terms. Therefore, even the truncated CC wavefunctions contain terms through all orders of z. In this sense, CC methods can be thought of a kind of resummation method. However, if the $\hat{T}$ series Eq. (27) is truncated, then only certain classes of MP terms are resummed while others are left truncated at low order in z. CCSD includes all MP3 terms and all terms at higher order of PT that involve only $\hat{T}_1$ and $\hat{T}_2$, CCSDT includes all MP5 terms and all higher-order terms involving only $\hat{T}_1$, $\hat{T}_2$, and $\hat{T}_3$, and so on.[74–76]

The CC method usually is better than the MPn method with comparable cost scaling, if the partial sum Eq. (10) without resummation is used for MPn; typically CCSD is more accurate than MP3 and CCSDT is more accurate than MP5. However, quadratic approximants reduce the MP5 error by a factor of approximately 2.5, which makes its accuracy comparable to that of CCSDT.[14]

There have been many attempts to develop CC methods with a cost scaling comparable to that of MP4 (proportional to N^7 where N is the basis dimension[77,d]). By far the most popular is the CCSD(T) method of Raghavachari et al.[78] This is a hybrid method, in which certain terms from MP4 and MP5, involving triple excitations, are added to the CCSD energy. CCSD(T) is usually more accurate than conventional MP4 partial summation[76] and on average appears to be almost as accurate as MP4qλ summation for atoms and for molecules at equilibrium geometries and more accurate if bonds are stretched.[44,63]

Can resummation methods be applied to the sequence of CC methods to obtain even higher accuracy without increasing computational cost? Empirical studies of the behavior of CC sequences have found patterns in the convergence that can be modeled with simple approximants. Consider the sequence

$$E^{(\mathrm{CC})} = E^{(\mathrm{HF})} + \delta_{\mathrm{SD}} + \delta_{(\mathrm{T})} + \dots \tag{29}$$

with

$$\begin{aligned} \delta_{\mathrm{SD}} &= E^{(\mathrm{CCSD})} - E^{(\mathrm{HF})}, \\ \delta_{(\mathrm{T})} &= E^{(\mathrm{CCSD(T)})} - E^{(\mathrm{CCSD})}. \end{aligned} \tag{30}$$

It has been found[63,65] that the convergence of this sequence can often be considerably improved with a

continued-fraction approximant,

$$E^{(\mathrm{CCSD(T)cf})} = \frac{E^{(\mathrm{HF})}}{1 - \frac{\delta_{\mathrm{SD}}/E^{(\mathrm{HF})}}{1-\delta_{(\mathrm{T})}/\delta_{\mathrm{SD}}}}. \tag{31}$$

This approximant, the CCSD(T)cf method, is not always reliable,[63,65,80,81] but it is possible to predict from the MP series classification the cases in which it will work well. For type-I systems, CCSD(T)cf has been found to be consistently more accurate than CCSD(T) and on average slightly more accurate than MP4qλ. For type-II systems, the MP4qλ [1/0,2] constrained approximant has been found to be on average the best of the methods if $|u_{\mathrm{n}}|$ is relatively large. Otherwise, various CCSD(T) resummations seem to give about equally good results. A [1/1] rational Padé approximant,

$$E^{(\mathrm{CCSD(T)r})} = E_0 + \frac{\delta_{\mathrm{SD}}}{1 - \delta_{(\mathrm{T})}/\delta_{\mathrm{SD}}}, \tag{32}$$

can also work well, as can a [0/0,1] quadratic approximant,[63]

$$E^{(\mathrm{CCSD(T)q})} = E_0 + \frac{\delta_{\mathrm{SD}}^2}{2\delta_{(\mathrm{T})}}\left[1 - (1 - 4\delta_{(\mathrm{T})}/\delta_{\mathrm{SD}})^{1/2}\right]. \tag{33}$$

Recommendations for optimal resummation strategies, depending on MP singularity structure, will be given in the section *Conclusions*.

A drawback of the CCSD(T)cf approximant is that it seems to be more sensitive than conventional CCSD(T) to the onset of multireference (MR) character as bonds are stretched,[65] although not nearly as sensitive as MP4qλ. All of these methods are expected to fail on the way to homolytic bond cleavage. For small displacements from the equilibrium bond distance, CCSD(T)cf was found to be the best of the methods, performing quite well, but for large displacements CCSD(T)cf failed sooner than did CCSD(T).[65] Whether this is due to a fortuitous concellation of errors in CCSD(T) or to a qualitative change in the CC convergence pattern is not clear.

Kenny et al.[79] proposed a continued fraction for the sequence HF, CCSD, CCSD(T), CCSDT in the form

$$E^{(\mathrm{CCSDTcf})} = E^{(\mathrm{HF})} + \frac{\delta_{\mathrm{SD}}}{1 - \frac{\delta_{(\mathrm{T})}/\delta_{\mathrm{SD}}}{1-\delta_{\mathrm{T}}^{(\mathrm{T})}/\delta_{(\mathrm{T})}}} \tag{34}$$

with

$$\delta_{\mathrm{T}}^{(\mathrm{T})} = E^{(\mathrm{CCSDT})} - E^{(\mathrm{CCSD(T))}}. \tag{35}$$

They found that this gave results that were about as accurate as the method of Brueckner doubles with perturbative treatment of quadruples, BD(TQ), which in principle improves the CC result by including contributions from quadruple excitations.[82] [However, Feller and Dixon[81] subsequently found that, at least for atomization energies, BD(TQ) was on average not any closer to FCI than was CCSD(T)cf.] Feller et al.[83,84] have found that the sequence CCSD, CCSDT, CCSDTQ can be reliably improved using the continued fraction

$$E^{(\mathrm{CCSDTQcf})} = E^{(\mathrm{HF})} + \frac{\delta_{\mathrm{SD}}}{1 - \frac{\delta_{\mathrm{T}}/\delta_{\mathrm{SD}}}{1-\delta_{\mathrm{Q}}/\delta_{\mathrm{T}}}} \tag{36}$$

with

$$\begin{aligned}\delta_{\mathrm{T}} &= E^{(\mathrm{CCSDT})} - E^{(\mathrm{CCSD})},\\ \delta_{\mathrm{Q}} &= E^{(\mathrm{CCSDTQ})} - E^{(\mathrm{CCSDT})}.\end{aligned} \tag{37}$$

Although CCSDTQ is very expensive to compute, it is significantly less expensive than FCI. Feller et al.[85] have used this CCSDTQcf method in numerous studies as a benchmark substitute for FCI.

The mathematical analysis of the sequences $E^{(HF)} + \delta_{\mathrm{SD}} + \delta_{\mathrm{T}} + \delta_{\mathrm{Q}} + \ldots$ and $E^{(HF)} + \delta_{\mathrm{SD}} + \delta_{(\mathrm{T})} + \ldots$ in terms of the properties of a function in the complex plane is considerably more murky than in the MP case. The energy as a function of the perturbation parameter z can be written in terms of the CC approximations as

$$\begin{aligned}E(z) \approx E_0 + E_1 z + z^2\delta_{\mathrm{SD}}(z) + z^4\delta_{\mathrm{T}}(z)\\ + z^6\delta_{\mathrm{Q}}(z) + \mathcal{O}(z^8),\end{aligned} \tag{38}$$

or, for CCSD(T),

$$\begin{aligned}E(z) \approx E_0 + E_1 z + z^2\delta_{\mathrm{SD}}(z)\\ + z^4\delta_{(\mathrm{T})}(z) + \mathcal{O}(z^5).\end{aligned} \tag{39}$$

The CC computations give the numerical values of the δ's at $z = 1$. Katz[16] considered the effect of exactly summing just certain classes of terms in $E(z)$ to infinite order for a related model problem. He showed that the result of this incomplete resummation was to qualitatively change the singularity structure, eliminating the branch points but introducing poles. He obtained an expansion essentially in the form of Eq. (38) and showed that the coefficient functions had poles in the negative half of the z plane. This expansion gave an excellent approximation to the exact solution except in the immediate vicinity of the branch points of the exact energy function and, of course, in the vicinity of the poles. Katz then argued that this would be a generic behavior for incomplete infinite-order summations of many-body perturbation theories.

Replacing the functions $\delta_{\mathrm{X}}(z)$ with their numerical values at $z = 1$ converts Eqs. (38) and (39) into asymptotic series about $z = 0$. However, these series are not asymptotic to the FCI energy function

but to some approximation to it. The continued fraction and the rational Padé approximant are functional forms containing poles. They are perhaps modeling the poles introduced by the incomplete infinite-order summations.

Another kind of application of Padé approximants to CC calculations was devised by Hirata and Bartlett.[15] They used rational approximants to improve the convergence of the CC iterations, treating the energy increments at each iteration as the 'series' coefficients.

OTHER APPLICATIONS

The focus here thus far has been on series approximations for the molecular electronic structure problem, and only on methods with the HF approximation as the reference solution. Other perturbation theories can be formulated for the electronic structure problem and for other aspects of molecular behavior, such as vibration and rotation. These have their own distinctive singularity structures, usually more complicated than that of the MP energy function.

Consider the quartic oscillator, with potential energy

$$V(x) = x^2 + bx^4, \tag{40}$$

as a model for molecular vibration, with the energy expanded in powers of b. The resulting series turns out to have a radius of convergence of zero,[86] due to an infinite sequence of branch points with limit point $b = 0$ in the complex b plane. Such complicated singularity structure is difficult to discern from a low-order series. However, if the series coefficients are known to very high order, then the ground-state eigenvalue series can be accurately resummed on the ground-state branch and on excited-state branches using algebraic approximants.[43,87,88]

Quadratic approximants are appropriate for summing coupling-constant perturbation series for vibrational spectra of polyatomic molecules. In addition to the singularity at the origin, these systems can have resonances, of two kinds: those that manifest themselves as avoided crossings of bound eigenstates as a function of the coupling constant, and those corresponding to metastable excited states embedded in the dissociation continuum. For the former, there are class-α branch points that can have a stronger effect than the singularity at the origin on the convergence at low and medium-high orders, and the series can be accurately summed with a quadratic approximant.[89] The latter have complex eigenvalues, with imaginary parts proportional to the spectral linewidths. Quadratic approximants place a branch point on the positive real axis between the origin and the physical value of the coupling constant, which makes the argument of the square root negative. The approximants give convergent results for both the real and the imaginary part.[90] If resonances are not present then rational Padé approximants work quite well.[91] Another way to deal with vibrational resonances is to find a similarity transform that reduces the coupling between the eigenstates,[92] followed by summation with rational approximants.

For atoms and molecules in external fields, PT in terms of the field strength would seem to be an obvious method to use. However, this too leads to a zero radius of convergence with a complicated singularity at the origin. Even the seemingly simple case of a hydrogen atom in a magnetic field, with potential energy $B^2(x^2 + y^2)/8 - r^{-1}$, has a strongly divergent perturbation series that cannot be efficiently summed with rational Padé approximants if the field strength parameter B is moderately large.[93] If the series coefficients are known to high order then the series can be summed using methods that model the rate of growth of the coefficients[94,95] or with a Borel transformation,[96] which expresses the energy as an integral of a function for which the Taylor series has a nonzero radius of convergence.

Resummation is especially important for semiclassical perturbation theories. These are theories that include the differential operators from the kinetic energy within the perturbation. The zeroth-order approximation has the system confined to the minimum of an effective potential energy surface, analogous to a classical mechanical description. The perturbation parameter can be the reciprocal of the particle mass, or Planck's constant, or, for a particularly flexible and general formulation, the dimensionality of space.[97] The resulting series have zero radius of convergence, due to a branch point at the origin.[46] However, for Coulombic systems the low-order behavior for the ground state is dominated by second-order pole[98–100] at a positive value of the perturbation parameter somewhat beyond the physical value and, for excited states, by square-root branch points.[101] For the ground state, the low-order convergence can be substantially improved simply by scaling the energy to make the pole explicit.[102]

CONCLUSIONS

Resummation methods work by making use of additional information about the mathematical structure of the theory. Information about the singularity

structure of the problem can be obtained by analysis of the eigenvalue equation or by analysis of the series coefficients. By constructing an approximant with the expected singularity structure, one can obtain a significantly more accurate estimate of the energy eigenvalue at no additional computational cost.

For Møller–Plesset PT, the general nature of the singularity structure is well understood. The singularities can be class-α isolated square-root branch points or class-β critical points. The relative positions of these singularities can be used to choose an appropriate resummation method. Tables 1 and 2 summarizethe results of a study in which resummed MP4 and CCSD(T) energies were compared with benchmark FCI values.[63] It is useful to consider three kinds of singularity structures:

> Class $\alpha|\alpha$. The dominant structure in both half-planes is of class α. This is typical of type-I electronic structure but also can occur in type-II systems with a basis set that is too compact to model a critical point. The optimal method for these systems, and for

TABLE 1 | Type-I Systems: Most Accurate Methods with N^7 Cost Scaling

System and Basis	MP4qλ	CCSD(T)	cf	r	q
BH cc-pVDZ	×		×		
BH aug-cc-pVQZ			×		
AlH cc-pVDZ	×	×	×	×	×
AlH aug-cc-pVQZ		×	×	×	×
CH_2 $\tilde{X}\,^3B_1$ DZP			×		
CH_2 $\tilde{a}\,^1A_1$ DZP			×		
CH_3 $\tilde{X}\,^2A_2''$ DZP	×		×		
NH_2 $\tilde{X}\,^2B_1$ DZP	×		×		
NH_2 $\tilde{A}\,^2A_1$ DZP	×		×		
H_2O^+ $\tilde{X}\,^2B_2$ cc-pVDZ	×		×		
H_2O^+ $\tilde{A}\,^2A_1$ cc-pVDZ	×		×		
F^- cc-pVDZ			×		
Ne cc-pVDZ	×		×		
N_2 cc-pVDZ			×		
C_2 cc-pVDZ				×	
CN^+ cc-pVDZ		×			

The indicated methods have error within 0.1 mE_h of the error from the most accurate method for that system. The 'cf', 'r', and 'q' columns are resummations of the HF, CCSD, CCSD(T) sequence (described in the section *Coupled-Cluster Theories*). The MP4qλ results are from the [1/0,1] approximant.

TABLE 2 | Type-II Systems: Most Accurate Methods with N^7 Cost Scaling

System and Basis	MP4qλ	CCSD(T)	avg	cf	avg	r	q	u_n
Class $\beta|x$								
Ar aug-cc-pVDZ	×							−6.50
Cl^- aug-cc-pVDZ	×							−3.32
HCl aug-cc-pVDZ	×							−3.19
H_2S cc-pVDZ	×							−3.06
Median absolute error (mE_h)	**0.157**	0.683		0.526		0.594	0.488	
Largest error (mE_h)	**0.229**	0.695		0.537		0.609	0.538	
Class $\beta|\alpha$								
HF cc-pVDZ				×				−2.67
F DZP			×		×		×	−2.49
Ne cc-pVTZ-(*f*)		×				×	×	−2.49
Ne aug-cc-pVDZ		×	×		×		×	−2.33
H_2O cc-pVDZ				×				−2.32
F^- cc-pVTZ-(*f*)	×						×	−2.04
HF cc-pVTZ-(*fld*)						×	×	−1.95
HF aug-cc-pVDZ				×				−1.90
F^- DZP						×		−1.42
F^- aug-cc-pVDZ				×				−1.36
Median absolute error (mE_h)	0.463	0.257	0.186	0.214	**0.218**	0.154	0.144	
Largest error (mE_h)	−2.165	0.735	0.366	−0.635	**0.302**	0.613	0.566	

The indicated methods have error within 0.1 mE_h of the error from the most accurate method for that system. The 'cf', 'r', and 'q' columns are resummations of the HF, CCSD, CCSD(T) sequence (described in the section *Coupled-Cluster Theories*). For the class-$\beta|\alpha$ systems, results are also shown for the average of CCSD(T) and CCSD(T)cf and for the average of CCSD(T)cf and CCSD(T)r. The MP4qλ results are from the constrained [1/0,2] approximant. The last column gives the dominant singularity at negative u of that approximant.

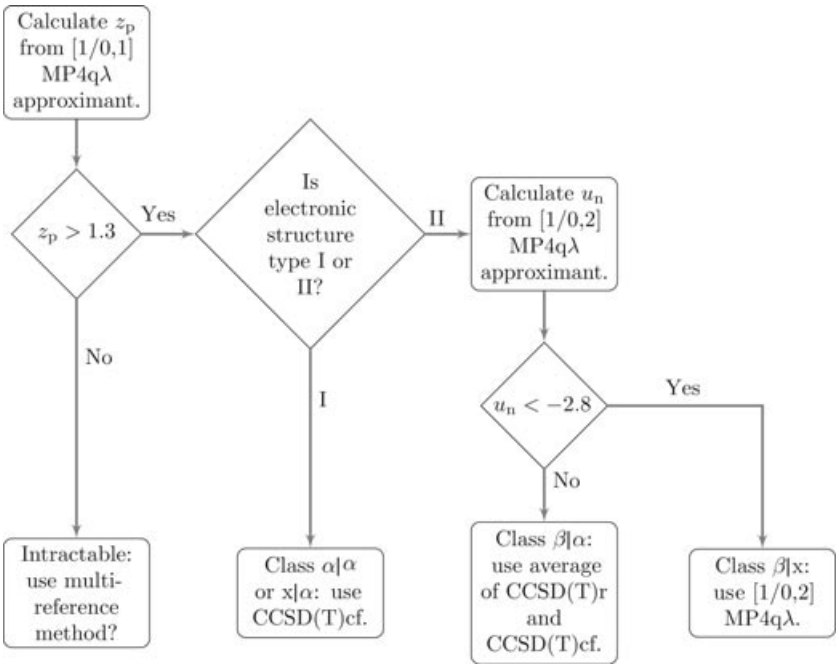

FIGURE 5 | A flowchart for choosing an appropriate method for an N^7 *ab initio* computation.

class-x|α, is usually the CC continued fraction CCSD(T)cf. The only exceptions in this benchmark set are C_2 and CN^+. These have significant MR character, which is evident from the fact that z_p, the dominant positive branch point from the MP4qλ approximant, is very close to $z = 1$, at 1.11 and 1.08, respectively.[33]

Class β|x. A dominant class-β singularity on the negative real axis with any singularity structure in the positive half-plane well beyond $z = 1$. These are type-II systems with u_n, the dominant singularity of the MP4qλ constrained [1/0,2] approximant, more negative than approximately −2.8. MP4qλ [1/0,2] is the optimal method.

Class $\beta|\alpha$. Type-II systems with $u_n > -2.8$. MP4qλ is usually not very effective here because the singularity structure in the positive half-plane becomes dominant before u_n can be shifted sufficiently far. The CC methods are to be preferred, but no single method is obviously the optimal choice for all cases. The average of the CCSDT(cf) and CCSDT(r) approximants appears to give consistently reliable results.

The flowchart in Figure 5 gives an algorithm for selecting the optimal N^7 method. This is based only on total energies and might need to be modified for properties such as atomization energies and vibrational frequencies. This is not a 'black-box'—it requires some subjective judgment. In particular, it is not always obvious whether to put a type-II system in class $\beta|\alpha$ or $\alpha|\alpha$. The Ne and F^- with the compact cc-pVDZ basis are in class $\alpha|\alpha$.[33] (Actually, Ne is better described as x|x, and is the only system here for which MP4 partial summation gives the best energy.) Note, however, that hydrogen fluoride with this same kind of basis is in class $\beta|\alpha$ because the basis is spread out over two atoms and this gives enough flexibility to model the class-β critical point. N_2, with a triple bond, is expected to be of type II, but analysis of the large-order series with the cc-pVDZ basis clearly shows it to be in class $\alpha|\alpha$. In contrast to hydrogen fluoride, the compact basis for N_2 is symmetric and therefore unable to model the class-β migration of valence electrons. The recommended class-$\alpha|\alpha$ method for this system gives agreement with the FCI energy within 0.350 mE_h, whereas the recommended class $\beta|\alpha$ method is in error by 0.844 mE_h.

Resummation of these N^7 methods apparently cannot by itself resolve the difficulty of modeling homolytic bond cleavage with a theory based on a single-reference zeroth-order approximation. This is a serious problem, as it can lead to large variations in accuracy over different regions of a potential energy surface. As bonds are stretched, this problem manifests itself in the MP4 singularity structure as a class-α singularity in negative half-plane that moves toward the origin and a positive class-α singularity that moves toward $z = 1$.

Various strategies for improving the underlying perturbation or CC theory have been proposed. The most straightforward is to include the effects of quadruple excitations, via MP6 (resummed with the Goldhammer–Feenberg transformation or with a quadratic approximant) or CCSDTQ (resummed with a continued fraction). However, the added computational cost is so high that these are feasible only for benchmark computations for small systems. The cost of coupled clusters with quadruple excitations can be be significantly reduced by retaining only those operators that are quadratic in the $\hat{T}_j$ in the expansion of $e^{\hat{T}}$.[103] This works well at equilibrium geometries but fails badly as bonds are stretched.

Another approach is to use a multireference perturbation theory (MRPT) or CC theory. With fourth-order MRPT, the singularity structure inferred from approximants could be used to optimize the choice of reference set. Too large a reference set is counterproductive due to intractable singularities caused by interaction of the reference set with with other excited states. (Such excited states are often called *intruder* states. A 'front-door intruder' corresponds to singular behavior in the positive half-plane while a 'back-door intruder' causes singular behavior in the negative half-plane.) A small reference set, carefully chosen, might work best.[4,104–109] However, the cost of fourth-order MRPT at present appears to be prohibitive.[4] Third order is too low to obtain useful estimates of singularity positions. However, Hose[110] has shown that multireference MP3 summed with a rational Padé approximant can give a reasonably accurate diatomic potential energy surface over a wide range of bond distances.

A less costly approach is to allow different orbitals for different electron spins. Using an unrestricted HF zeroth-order approximation gives the correct dissociation limit, and the accuracy of unrestricted MP4 can be improved with resummation, but the accuracy at intermediate bond distance is poor.[63,65] *Z*-averaged PT[111,112] seems to be a more promising way to implement this idea. Another possibility might be to replace the HF optimized zeroth-order wavefunctions with approximate wavefunctions optimized at MP2 with a scale factor multiplying the opposite-spin component of the second-order energy[113] and then use this as the starting point for a higher-order perturbation series.

A fourth approach is to use an unconventional partitioning of the Hamiltonian. There are infinitely many ways to do this, which allows for much creativity. A systematic strategy is to directly manipulate the spacings of energy levels at zeroth order.[54–56,114,115] By adjusting the spacings, class-α singularities, which correspond to crossings of low-lying excited states with the ground state, could in principle be shifted to less harmful positions. Another strategy, which works well with semiclassical PT,[117,118] is to scale the interelectron repulsion potential with a function of the perturbation parameter. It is *not* necessarily the best strategy to make the zeroth-order approximation resemble the physical solution as closely as possible.[119] It is quite possible that a less accurate zeroth-order energy spectrum will result in a perturbation series more amenable to resummation.

NOTES

[a]For an alternative derivation, see Ref 17.
[b]This is a special case of a more general theorem that was derived earlier by mathematicians, see Ref 18.
[c]For a quantum mechanical collection of particles, the definition of the 'volume of the system' needs to be handled with some care. See Ref 20.
[d]Although MP4 and CCSD(T) formally scale as N^7, in practice, the scaling power is closer to 4. See, for example, Ref 77.

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