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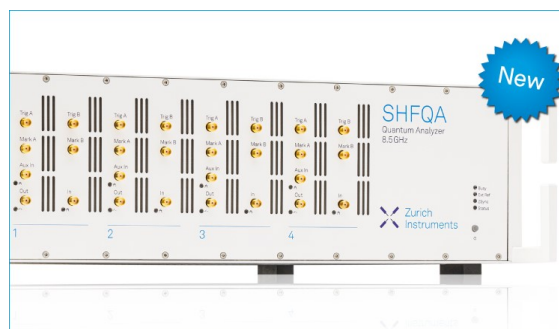
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Convergent summation of Møller–Plesset perturbation theory

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Rational and algebraic Padé approximants are applied to Møller–Plesset (MP) perturbation expansions of energies for a representative sample of atoms and small molecules. These approximants can converge to the full configuration–interaction result even when partial summation diverges. At order MP2 (the first order beyond the Hartree–Fock approximation), the best results are obtained from the rational [0/1] Padé approximant of the total energy. At MP3 rational and quadratic approximants are about equally good, and better than partial summation. At MP4, MP5, and MP6, quadratic approximants appear to be the most dependable method. The success of the quadratic approximants is attributed to their ability to model the singularity structure in the complex plane of the perturbation parameter. Two classes of systems are distinguished according to whether the dominant singularity is in the positive half plane (class A) or the negative half plane (class B). A new kind of quadratic approximant, with a constraint on one of its constituent polynomials, gives better results than conventional approximants for class B systems at MP4, MP5, and MP6. For CH₃ with the C–H distance at twice the equilibrium value the quadratic approximants yield a complex value for the ground-state electronic energy. This is interpreted as a resonance eigenvalue embedded in the ionization continuum. © 2000 American Institute of Physics. [S0021-9606(00)30208-2]

I. INTRODUCTION

Møller–Plesset perturbation theory (MPPT)¹ is currently one of the most widely used methods of *ab initio* quantum chemistry. However, recent studies have suggested that the Møller–Plesset expansion might often be insufficiently convergent to yield dependable results.^{2–8} The zeroth-order of MPPT is the Hartree–Fock approximation, described by the Fock operator, \hat{F} . The Hamiltonian \hat{H} is partitioned as

$$\hat{H} = \hat{F} + z\hat{\phi}, \quad \hat{\phi} = \hat{H} - \hat{F}, \quad (1)$$

where z is treated as a perturbation parameter with the physical solution corresponding to $z_{\text{phys}} = 1$. The resulting energy eigenvalues are functions of z with asymptotic expansions

$$E(z) = \sum_{j=0}^{\infty} E_j z^j. \quad (2)$$

$E(z)$ can be estimated from *partial summation* of the asymptotic series, in terms of the summation approximants

$$S_n(z) = \sum_{j=0}^n E_j z^j. \quad (3)$$

S_0 is the Hartree–Fock approximation. S_1 is generally called “second-order Møller–Plesset theory” (MP2). Similarly, S_2 is referred to as MP3, S_3 as MP4, and so on. Computer programs are available for direct calculation of the E_j for j from 0 to 5,⁹ although the computational cost increases significantly with j . For $j > 5$ the E_j can be extracted from configuration–interaction calculations.^{4,10,11}

The recent studies^{2–8} have demonstrated that the convergence of the sequence S_n can be unsteady. In particular, the studies by Olsen, Christiansen, and co-workers^{4,5} indicate

that S_n can be a divergent sequence, so that S_n will not approach the correct result even in the limit $n \rightarrow \infty$. Partial summation is divergent if there exists a singularity in the function $E(z)$ (a pole, a branch point, or an essential singularity) within the circle $z = |z_{\text{phys}}|$ in the complex z plane.¹² For MPPT, the singularity responsible for the divergence is expected to be a two-sheet branch point^{5,13} connecting the physical eigenvalue (i.e., the eigenvalue that approaches E_0 in the limit $z \rightarrow 0$) to a branch of $E(z)$ corresponding to the eigenvalue of an “intruder state.” The intruder state is an excited state that becomes stabilized at nonphysical values of z , becoming degenerate with the physical state at a value z_s corresponding to a branch-point singularity. In the case of MPPT for Ne, Christiansen *et al.*⁵ showed that at $z \approx -0.82$ the ground-state energy is equal to the energy of a state described by a wave function dominated by contributions from quintuple and higher excitations.

The sequence S_n can have poor convergence because the functions $S_n(z)$ are polynomials, which are nonsingular at all finite z and therefore can describe the singular function $E(z)$ only with limited accuracy. It is reasonable to expect that better results can be obtained by replacing the S_n with approximants that have a singularity structure resembling that of $E(z)$. A class of multiple-valued approximants with branch-point singularities was devised by Padé over 100 years ago.¹⁴ These are *algebraic approximants*, which are algebraic generalizations of the rational approximants usually associated with his name. Algebraic summation approximants are not widely known, although their mathematical properties have been studied in some detail^{15–19} and they have been applied in recent years to a variety of problems including, for example, the calculation of complex eigenvalues for the H atom in an electric field²⁰ and resonance ener-

gies in molecular vibration–rotation spectra.^{21–23} Here quadratic approximants (algebraic approximants of degree 2) will be applied to MP6 expansions calculated by He and Cremer³ for a representative set of atoms and small molecules and to large-order expansions of Olsen *et al.*⁴

II. METHOD

The familiar rational Padé approximants,

$$S_{[L/M]}(z) = P_L(z)/Q_M(z), \quad (4)$$

are ratios of polynomials P_L , Q_M , of degrees L , M , that satisfy the linear equation^{14,24}

$$Q_M E - P_L \sim O(z^{L+M+1}). \quad (5)$$

The notation “ $\sim O(z^m)$ ” means that the asymptotic expansion of the left-hand side of the equation contains no terms proportional to powers of z of degree less than m . (This formulation of $S_{[L/M]}$ differs slightly from that used by Bartlett and Shavitt,²⁵ in which the correlation energy, $E - E_0$, is summed rather than the total energy E .) By convention, $Q_M(0)$ is defined to be 1. The remaining M coefficients of Q_M and the $L+1$ coefficients of P_L are determined by the set of linear equations obtained by collecting terms in Eq. (5) according to powers of z .

Suppose we replace Eq. (5) with the quadratic equation

$$Q_M E^2 - P_L E + R_N \sim O(z^m). \quad (6)$$

The approximants for E are then

$$S_{[L/M,N]}(z) = \frac{1}{2} \left[\frac{P_L}{Q_M} \pm \frac{1}{Q_M} (P_L^2 - 4Q_M R_N)^{1/2} \right]. \quad (7)$$

The functions $S_{[L/M,N]}(z)$ have two branches connected by branch-point singularities at the values of z that are roots of the discriminant polynomial $P_L^2 - 4Q_M R_N$.

Let

$$P_L = \sum_{i=0}^L p_i z^i, \quad Q_M = 1 + \sum_{i=1}^M q_i z^i, \quad R_N = \sum_{i=0}^N r_i z^i. \quad (8)$$

The $L+M+N+2$ coefficients p_i , q_i , r_i can be determined from Eq. (6) with $m=L+M+N+2$, by collecting terms according to powers of z . To calculate $S_{[L/M,N]}$ the perturbation expansion, Eq. (2), must be known through order $n=L+M+N+1$. This is the approach used in previous studies of quadratic approximants. For the lowest-order approximant, $S_{[0/0,0]}$, the solution is $p_0=2E_0$, $r_0=E_0^2$, which implies that the discriminant is identically zero, and $S_{[0/0,0]}=E_0$ for both branches. Branch points are present for $n \geq 2$.

Alternatively, the value of p_0 or r_0 can be assigned as an arbitrary parameter. Then m in Eq. (6) is $L+M+N+1$ and $S_{[L/M,N]}$ is determined from order $n=L+M+N$. If r_0 is the parameter, then the zeroth-order solution is

$$S_{[0/0,0]} = \begin{cases} E_0, \\ r_0/E_0. \end{cases} \quad (9)$$

If the order n is large, the performance of either of these two approximant schemes should be about the same. At low orders the performance may differ; presumably, the scheme that at lowest order most accurately describes the qualitative

spacing at $z=z_{\text{phys}}$ of the energy levels involved in the dominant branch point will be the one that gives the best results. The singularity structure that has been identified for MPPT for Ne,⁵ involving the ground state and a highly excited state, suggests the use of a constrained approximant scheme with $r_0=0$. Then, according to Eq. (9), the ground-state energy will be initially set to the Hartree–Fock value, E_0 , while the excited state will initially be assigned an energy of zero, so that the energy of the excited state will be approached from above. The conventional unconstrained approximants should be best for cases in which the branch point involves states that have nearly the same energy at $z=z_{\text{phys}}$.

III. CONVERGENCE AT LARGE ORDER

To study the large-order behavior of MPPT, Handy *et al.*¹⁰ and Laidig *et al.*¹¹ carried out full configuration–interaction (FCI) calculations for various small molecules and in the course of the computations took advantage of the intermediate iterations to estimate the MP energy expansion coefficients up to very large orders. They concluded that the partial sums of the expansions were convergent, although the initial convergence in some cases was slow and uneven for eigenstates not dominated by a single configuration. Recently, Olsen and co-workers^{4,5} carried out similar calculations but with augmented basis sets and found that the MP expansions even for the single configuration dominated systems Ne, F⁻, HF, and H₂O in fact diverged if the basis set included functions capable of describing diffuse excited states. The case of Ne was studied in detail⁵ and the divergence was attributed to an avoided crossing between the ground state and an excited state at $z \approx -0.82$, with the wavefunction for the excited state dominated by contributions from quintuple and higher excitations.

In principle, the MP expansion should converge to the FCI energy. Figure 1 shows the quantity $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, which is a continuous measure of the number of accurate digits, vs the order n of the perturbation expansion for Ne. Results are shown for four different summation approximant sequences S : the partial sums, S_n ; the rational Padé approximant sequence $S_{[0/0]}, S_{[0/1]}, S_{[1/1]}, \dots$; the unconstrained quadratic Padé approximant sequence $S_{[0/0,0]}, S_{[1/0,0]}, S_{[1/0,1]}, S_{[1/1,1]}, \dots$; and the quadratic approximants with $r_0=0$, in the same index sequence.

As stressed by Olsen *et al.*,⁴ the behavior of the partial sums can depend strongly on the nature of the basis set. The two panels of Fig. 1 correspond to results from different basis sets. With the correlation-consistent polarized valence double zeta basis (cc-pVDZ)²⁶ the partial sums converge reasonably well, but with the more accurate aug-cc-pVDZ basis,²⁷ which is augmented with diffuse functions, the partial sums at first seem to converge, with closest approach to E_{FCI} at MP15, where $S_{14} - E_{\text{FCI}} = 0.000142$ hartree, but then gradually diverge. The rational approximants, the unconstrained quadratic approximants, and the $r_0=0$ quadratic approximants converge to the FCI limit for either basis set.

In the quadratic approximants the root of the discriminant polynomial nearest the origin of the complex z plane should converge to the location of the dominant branch

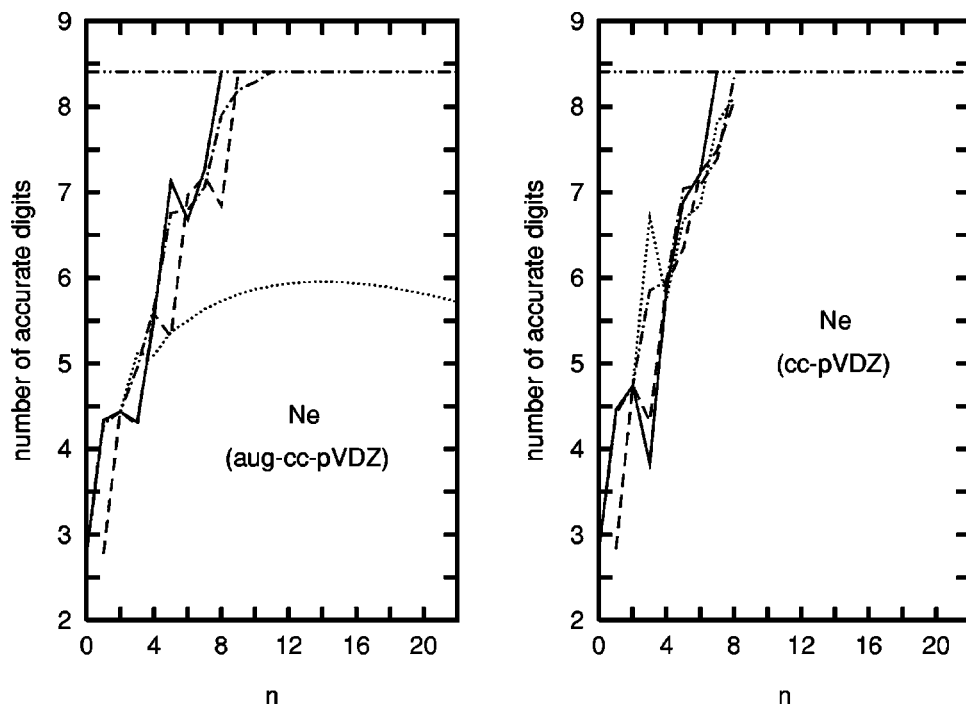


FIG. 1. Convergence of summation approximations for the ground-state energy of Ne. The curves show $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, where S is the value of the summation approximant. The summation methods are partial sums (dotted curve), rational summation (solid curve), unconstrained quadratic summation (dashed curve), and constrained ($r_0=0$) quadratic summation (dashed-dotted curve). The expansion coefficients are from Ref. 4. The basis set used for the expansion in the left panel is the aug-cc-pVDZ (frozen core) basis, which is augmented with diffuse functions.²⁷ The right panel uses the cc-pVDZ (frozen core) basis without the diffuse functions.²⁶ The FCI energies, E_{FCI} , are $-128.709\,476$ hartree and $-128.679\,025$, respectively. The dash-dot-dot lines indicate the precision of E_{FCI} .

point, z_s . For the aug-cc-pVDZ Ne expansion, the quadratic approximants by order $n=6$ consistently place z_s in the general vicinity of -1 . At $n=20$ the branch point position begins to stabilize at -0.8 . In contrast, with the cc-pVDZ basis the root nearest to the origin is at approximately $-2 \pm i$. Clearly, for this system the diffuse functions are needed to describe the intruder state responsible for the branch point within the circle of convergence. While this branch point

strongly affects the convergence of the partial sums, it has little effect on the convergence of the three kinds of Padé approximants.

Figure 2 shows results for F^- , with the aug-cc-pVDZ basis. This is an especially difficult system for the partial sums, which diverge rapidly for $n > 3$. The quadratic approximants place a branch point at -0.61 .

He and Cremer²⁸ have designated systems as “class A” or “class B” according to the sign patterns of the E_i and have offered an interpretation of this classification in terms of patterns of electron localization.²⁹ For class A systems the E_i have same sign for all i while for class B systems the E_i at some point begin to alternate in sign. If the E_j strictly alternate in sign in the limit of large j then the dominant branch point must lie on the negative real axis. If they have the same sign then the branch point lies on the positive real axis. If the dominant branch points are a complex-conjugate pair in the negative half plane, then there will be regions of alternating signs with the pattern broken periodically by consecutive E_j of the same sign.³⁰ The period is

$$n_0 = \pi / \arctan(|\mathcal{I}z_s / \mathcal{R}z_s|). \quad (10)$$

If the dominant branch points are complex conjugates in the positive half plane, then there will be regions of only one sign alternating with regions of only the opposite sign. It seems reasonable to define class A systems as those for which the dominant singularity is in the positive half plane and class B systems as those for which the dominant singularity is in the negative half plane, in order to extend the classification scheme to systems with complex-conjugate dominant branch points. Note that branch points that do not lie on the real axis must occur in complex-conjugate pairs in order to be consistent with the fact that the E_j are real numbers.

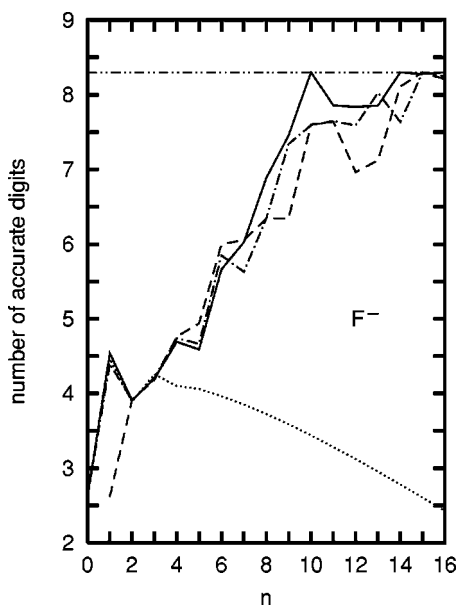


FIG. 2. Convergence of summation approximations for the ground-state energy of F^- . The curves show $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, where S is the value of the summation approximant. The summation methods are partial sums (dotted curve), rational summation (solid curve), unconstrained quadratic summation (dashed curve), and constrained ($r_0=0$) quadratic summation (dashed-dotted curve). The expansion coefficients, from Ref. 4, were calculated with the aug-cc-pVDZ (frozen core) basis set. The FCI result is $E_{\text{FCI}} = -99.669\,369$ hartree.

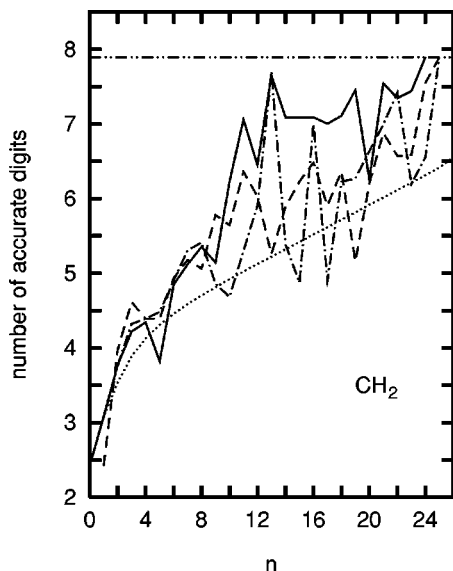


FIG. 3. Convergence of summation approximants for the ground-state energy of CH_2 . The curves show $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, where S is the value of the summation approximant. The summation methods are partial sums (dotted curve), rational summation (solid curve), unconstrained quadratic summation (dashed curve), and constrained ($r_0=0$) quadratic summation (dashed-dotted curve). The expansion coefficients, from Ref. 4, were calculated with the aug-cc-pVDZ (frozen core) basis set. The FCI result is $E_{\text{FCI}} = -39.032\,446$ hartree.

Figure 3 shows results for CH_2 , which is a class A system. The quadratic approximants place a branch point in the neighborhood of 1.3. (At a few orders the approximants see this as a complex-conjugate pair at approximately $1.2 \pm 0.1i$.) Since z_s is outside of the circle $|z|=1$, the partial sums are convergent, but the convergence is rather slow. All three kinds of Padé approximants converge much faster, but the convergence of the quadratic Padé approximants for $n > 8$ is uneven. The reason for this seems to be the placement of spurious branch points near z_{phys} . For example, for the unconstrained quadratic results in Fig. 3 the accuracy is less than or about equal to that of the partial sums only at $n = 13$ and 19. At $n = 13$ the quadratic approximant has spurious branch points at 0.913 and 0.917. At $n = 19$ there is a spurious branch point at 0.949.

In general, the number of branch points in the $S_{[L/M,N]}$ approximant will be either $2L$ or $M+N$, whichever is greater. If there is only one branch point that is significantly affecting the expansion divergence, then the remaining branch points will be nonphysical. Ideally, they will be placed far from the origin or they will occur in almost coincident pairs. However, their positions can vary greatly from order to order and a nonphysical branch point close to z_{phys} can seriously degrade the accuracy. There seems to be a tendency for the spurious branch points to appear in the vicinity of the dominant branch point, which implies that the large-order convergence of quadratic approximants will in general be steadier for class B systems than for class A systems. The rational approximants model a branch point by tracing a branch cut with a sequence of poles.²⁴ Spurious poles affect the accuracy of rational Padé approximants, but

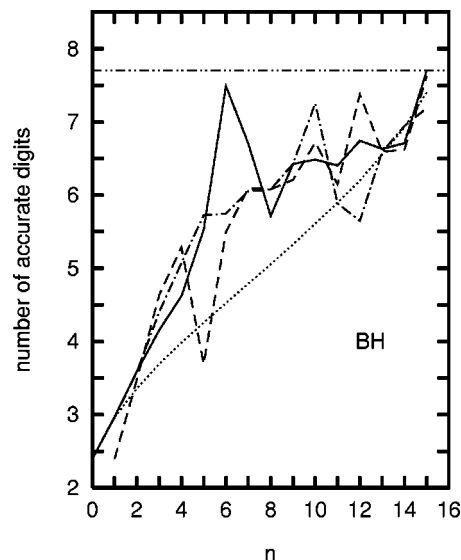


FIG. 4. Convergence of summation approximants for the ground-state energy of BH . The curves show $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, where S is the value of the summation approximant. The summation methods are partial sums (dotted curve), rational summation (solid curve), unconstrained quadratic summation (dashed curve), and constrained ($r_0=0$) quadratic summation (dashed-dotted curve). The expansion coefficients, from Ref. 4, were calculated with the aug-cc-pVDZ (frozen core) basis set. The FCI result is $E_{\text{FCI}} = -25.218\,277$ hartree.

these are less likely because many poles can be employed to model a single branch point.

Figure 4 shows results for the BH molecule. This is a class A system. The dominant branch point of the quadratic approximants is reasonably stable through 10th order, con-

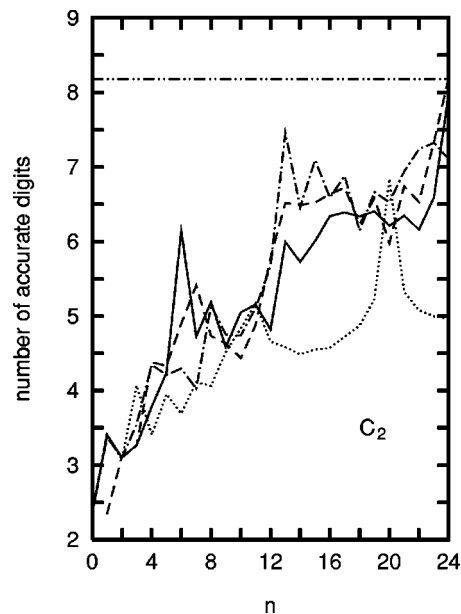


FIG. 5. Convergence of summation approximants for the ground-state energy of C_2 . The curves show $-\log_{10} |(S - E_{\text{FCI}})/E_{\text{FCI}}|$, where S is the value of the summation approximant. The summation methods are partial sums (dotted curve), rational summation (solid curve), unconstrained quadratic summation (dashed curve), and constrained ($r_0=0$) quadratic summation (dashed-dotted curve). The expansion coefficients, from Ref. 4, were calculated with the aug-cc-pVDZ (frozen core) basis set. The FCI result is $E_{\text{FCI}} = -75.730\,209$ hartree.

verging to approximately 1.6. Starting at 11th order the position of the branch point becomes unstable. At 15th order the unconstrained approximant, which gives full agreement with the FCI energy, places the branch point at $1.5 \pm 0.2i$. Since $|z_s|$ is relatively large in this case, z_{phys} is well within the circle of convergence and hence the partial sums converge rather well, although their accuracy is usually somewhat lower than that of the other approximants. The poor result from the unconstrained quadratic approximant at order 5 is due to a spurious branch point at 1.006.

Figure 5 shows results for the C_2 molecule. The singularity structure of the quadratic approximants is quite stable in this case with the dominant branch points at $-0.97 \pm 0.34i$ and another branch point pair at $1.18 \pm 0.36i$. Because z_{phys} is just barely inside the circle of convergence, the partial sums can be expected to converge at large order but the convergence will be very slow.

IV. CONVERGENCE AT LOW ORDER

In practice, the most important question is how best to sum the MP expansion at low orders. The usual motivation for using MPPT is that its computational cost is significantly less than that of other *ab initio* methods that include electron correlation. The large-order expansions considered in Sec. III do not offer this cost advantage, since they require an FCI calculation to obtain the MP expansion coefficients. Direct calculations of the E_i can currently be carried out through MP6.^{29,31} He and Cremer³ have tabulated MP6 expansions for a variety of atoms and small molecules. Table I compares the convergence error from partial summation, rational Padé summation, and quadratic Padé summation for a representative sample of 16 of their expansions. The results are analyzed in Table II.

Table II compares the summation methods for the total sample of systems but also breaks down the results according to the two classes. (H_2O with $R=2R_e$ has branch points on the both the positive and the negative real axes, approximately equidistant from the origin. It is grouped with class B because the E_j alternate in sign, indicating that the singularity at negative z is dominant at these orders.) For MP2 the rational approximants are in all cases the most accurate, although, with the single exception of F^- , the improvement over the other methods is relatively small. For MP3 the rational and the quadratic approximants are about equal in accuracy and almost always better than partial summation, although in general this advantage is significant only for class A systems. For class A systems at MP4 the quadratic and rational approximants are about equal in accuracy and almost always significantly better than partial summation. However, for class B systems at MP4 the rational Padé summation is consistently the worst of the methods while the constrained quadratic summation is usually the best. At MP5 and MP6 partial summation is usually the worst of the methods, both for class A and for class B. The constrained quadratic approximants are usually the best method for class B. For class A systems at MP5 the unconstrained quadratic approximants are best. For class A at MP6 all three Padé methods are about equally successful.

For a class A system the intruder state can be expected to be closer in energy to the physical state than in the case of a class B system, where the crossing occurs at a highly non-physical negative value of z . Therefore, according to the discussion in Sec. II, the unconstrained quadratic approximants at low orders should be relatively better for class A systems while the approximants with $r_0=0$ will be relatively better for class B. In practice, the advantage of the $r_0=0$ approximants for class B is not apparent until MP4. At MP2 and MP3, the contributions to the E_j from the singularities evidently are obscured by nonsingular contributions.

V. RESONANCE EIGENVALUES

For one of the systems studied by He and Cremer,³ CH_3 with the C–H distance set at twice the equilibrium bond distance, the quadratic approximants converge to a complex number. (This case was not included in Tables I and II.) The total energy for this system as given by the various summation methods is shown in Table III.

Vainberg *et al.*²⁰ have demonstrated that perturbation expansions for energy eigenvalues of the H atom in an external electric field converge to a complex energy when summed with quadratic approximants, even though the expansion coefficients are real. The H atom is unstable in an electric field. The real part of this complex energy eigenvalue is the energy of a resonance in the $e^- + H^+$ scattering continuum. The imaginary part is a measure of the resonance width, $\Gamma = 2|IE|$, with the resonance lifetime given by $4\hbar/\Gamma$.³⁷ Such resonances correspond to a complex-conjugate pair of eigenvalues. One of the eigenvalues corresponds to outgoing boundary conditions while the other corresponds to incoming boundary conditions. These two solutions are connected by a branch point on the positive real axis. Quadratic approximants have also been used to calculate complex eigenvalues for shape resonances²¹ and molecular predissociation resonances.^{21,22}

The convergence of the MPPT to a complex energy suggests that CH_3 with C–H distance $R=2R_e$ is a resonance in the $e^- + CH_3^+$ continuum, with energy -39.172 hartree and width 0.042 hartree. The convergence of the unconstrained quadratic approximants is faster than that of the $r_0=0$ approximants, as expected from the discussion in Sec. II. There is a stable branch point in the quadratic approximants at 0.71. Apparently, the stronger electron correlation in CH_3 causes its energy to rise above that of the cation as z increases.

VI. DISCUSSION

Comparison of the accuracy of various kinds of summation approximants, using MP6 expansions for 16 representative atoms and molecules, leads to the following recommendations:

- MP2 should be summed with a rational [0/1] Padé approximant.
- MP3 should be summed with unconstrained quadratic Padé approximants.

TABLE I. $S - E_{\text{FCI}}$, in hartree, where S is a summation approximant of indicated type and order for Møller–Plesset perturbation theory. Numbers in parentheses come from approximants that have a branch point within a distance of 0.2 from the point $z=1$. The value shown for z_s is the position of the branch point nearest the origin in the most accurate of the quadratic approximants at MP6. The expansion coefficients are from Ref. 3.

Order	Partial sum	Rational Padé	Quadratic Padé, unconstrained	Quadratic Padé, $r_0=0$
BH, $R=R_e$	$E_{\text{FCI}} = -25.2276^a$	$E_{\text{corr}} = 0.102\ 355$	$z_s = 1.4$	
MP2	0.028 627	0.028 410	0.102 355	0.028 842
MP3	0.011 049	0.005 546	(-0.018 983)	0.005 662
MP4	0.005 048	0.001 932	0.000 227	0.001 079
MP5	0.002 514	0.000 316	-0.000 078	0.000 288
MP6	0.001 293	-0.000 039	-0.000 195	0.000 008
BH, $R=2R_e$	$E_{\text{FCI}} = -25.127\ 33^a$	$E_{\text{corr}} = 0.139\ 132$	$z_s = 1.7$	
MP2	0.052 830	0.052 531	0.139 132	0.053 126
MP3	0.027 112	0.016 195	(-0.005 670 ± 0.063 449 i)	0.016 449
MP4	0.013 328	-0.002 672	(-0.031 314 ± 0.047 400 i)	-0.009 516
MP5	0.006 054	-0.002 079	-0.005 416	-0.000 642
MP6	0.002 186	-0.002 181	-0.002 323	-0.002 337
NH ₂ ² B ₁ , $R=R_e$	$E_{\text{FCI}} = -55.742\ 62^b$	$E_{\text{corr}} = 0.165\ 438$	$z_s = 2.1$	
MP2	0.022 172	0.021 802	0.165 438	0.022 539
MP3	0.006 215	0.004 215	0.001 202	0.004 273
MP4	0.001 900	0.000 283	-0.000 480	0.000 438
MP5	0.000 765	0.000 360	0.000 259	0.000 344
MP6	0.000 336	0.000 301	0.000 104	0.000 129
NH ₂ ² B ₁ , $R=2R_e$	$E_{\text{FCI}} = -55.505\ 52^b$	$E_{\text{corr}} = 0.111\ 898$	$z_s = 2.0$	
MP2	0.036 528	0.036 425	0.111 898	0.036 630
MP3	0.022 472	0.019 250	0.011 673	0.019 285
MP4	0.018 796	0.017 493	0.016 979	0.017 207
MP5	0.017 486	0.016 489	0.016 366	0.016 712
MP6	0.016 688	0.025 570	(0.020 764)	0.017 317
NH ₂ ² A ₁ , $R=R_e$	$E_{\text{FCI}} = -55.688\ 76^b$	$E_{\text{corr}} = 0.162\ 380$	$z_s = 2.1$	
MP2	0.020 290	0.019 925	0.162 380	0.020 652
MP3	0.005 445	0.003 713	0.001 184	0.003 766
MP4	0.001 617	0.000 271	-0.000 332	0.000 419
MP5	0.000 651	0.000 325	0.000 246	0.000 318
MP6	0.000 275	0.000 281	0.000 085	0.000 114
NH ₂ ² A ₁ , $R=2R_e$	$E_{\text{FCI}} = -55.415\ 13^b$	$E_{\text{corr}} = 0.154\ 402$	$z_s = 1.3$	
MP2	0.065 312	0.065 168	0.154 402	0.065 455
MP3	0.047 064	0.042 364	0.029 370	0.042 422
MP4	0.040 303	0.036 314	0.033 295	0.035 619
MP5	0.037 016	0.033 392	0.032 110	0.033 336
MP6	0.034 810	-0.017 356	0.036 710	0.033 255
CH ₃ , $R=R_e$	$E_{\text{FCI}} = -39.721\ 21^c$	$E_{\text{corr}} = 0.150\ 583$	$z_s = 2.3$	
MP2	0.025 262	0.024 864	0.150 583	0.025 656
MP3	0.006 361	0.003 004	-0.003 199	0.003 101
MP4	0.001 981	0.000 655	0.000 129	0.000 428
MP5	0.000 770	0.000 273	0.000 216	0.000 240
MP6	0.000 346	-0.000 025	(-0.000 611)	0.000 172
CH ₂ ³ B ₁	$E_{\text{FCI}} = -39.046\ 26^d$	$E_{\text{corr}} = 0.113\ 215$	$z_s = 1.5$	
MP2	0.020 925	0.020 706	0.113 215	0.021 143
MP3	0.005 547	0.002 472	-0.003 794	0.002 535
MP4	0.001 880	0.000 730	0.000 297	0.000 501
MP5	0.000 784	0.000 242	0.000 188	0.000 260
MP6	0.000 364	-0.000 028	-0.000 080	0.000 349
CH ₂ ¹ A ₁	$E_{\text{FCI}} = -39.027\ 18^d$	$E_{\text{corr}} = 0.140\ 886$	$z_s = 1.2$	
MP2	0.031 056	0.030 745	0.140 886	0.031 364
MP3	0.010 590	0.005 903	-0.005 105	0.006 010
MP4	0.004 979	0.002 855	0.001 925	0.002 404
MP5	0.002 949	0.001 514	0.001 315	0.001 687
MP6	0.001 977	0.000 501	0.000 203	(0.003 444)
Ne	$E_{\text{FCI}} = -128.767\ 89^e$	$E_{\text{corr}} = 0.224\ 066$	$z_s = -2.1$	
MP2	0.003 830	0.003 452	0.224 066	0.004 206
MP3	0.005 377	0.005 366	0.005 356	0.005 364
MP4	-0.000 650	0.003 919	0.004 146	-0.000 854
MP5	0.000 827	0.000 440	0.000 346	0.000 337
MP6	-0.000 368	-0.000 100	0.000 560	-0.000 102

TABLE I. (Continued.)

Order	Partial sum	Rational Padé	Quadratic Padé, unconstrained	Quadratic Padé, $r_0=0$
F	$E_{\text{FCI}} = -99.594\ 88^{\text{f}}$ $E_{\text{corr}} = 0.194\ 894$ $z_s = -2.1$			
MP2	0.013 123	0.012 790	0.194 894	0.013 454
MP3	0.004 941	0.004 555	0.004 109	0.004 572
MP4	0.000 529	-0.005 051	(-0.007 031)	-0.000 319
MP5	0.000 461	0.000 349	0.000 263	0.000 197
MP6	0.000 020	0.000 042	-0.000 047	0.000 007
F ⁻	$E_{\text{FCI}} = -99.706\ 69^{\text{g}}$ $E_{\text{corr}} = 0.262\ 994$ $z_s = -0.65$			
MP2	0.000 588	-0.000 106	0.262 994	0.001 277
MP3	0.013 851	0.013 213	0.012 659	0.013 183
MP4	-0.005 398	0.005 777	0.006 064	-0.005 213
MP5	0.006 671	0.001 833	0.001 458	0.001 611
MP6	-0.006 928	-0.003 697	0.000 529	-0.002 733
HF, $R=R_e$	$E_{\text{FCI}} = -100.250\ 97^{\text{a}}$ $E_{\text{corr}} = 0.203\ 882$ $z_s = -1.6$			
MP2	0.007 804	0.007 419	0.203 882	0.008 187
MP3	0.005 438	0.005 409	0.005 379	0.005 414
MP4	-0.000 264	0.008 481	0.009 507	-0.000 838
MP5	0.000 859	0.000 536	0.000 435	0.000 385
MP6	-0.000 230	0.000 020	-0.000 546	-0.000 004
HF, $R=2R_e$	$E_{\text{FCI}} = -100.081\ 11^{\text{a}}$ $E_{\text{corr}} = 0.263\ 536$ $z_s = -1.1$			
MP2	0.024 045	0.023 469	0.263 536	0.024 617
MP3	0.026 959	0.026 924	0.026 890	0.026 917
MP4	0.004 840	0.023 946	0.024 385	0.000 718
MP5	0.008 103	0.006 043	0.004 069	0.003 878
MP6	-0.001 131	-0.003 477	0.010 759	-0.004 897
H ₂ O, $R=R_e$	$E_{\text{FCI}} = -76.256\ 62^{\text{a}}$ $E_{\text{corr}} = 0.216\ 083$ $z_s = -2.2$			
MP2	0.012 966	0.012 422	0.216 083	0.013 506
MP3	0.007 223	0.007 056	0.006 873	0.007 073
MP4	0.000 820	0.035 588	0.023 707 ± 0.030 954 <i>i</i>	-0.000 206
MP5	0.000 704	0.000 493	0.000 288	0.000 247
MP6	0.000 078	0.000 045	-0.000 142	0.000 005
H ₂ O, $R=2R_e$	$E_{\text{FCI}} = -100.187\ 56^{\text{a}}$ $E_{\text{corr}} = 0.369\ 984$ $z_s = -1.7, 1.7$			
MP2	0.053 667	0.052 661	0.369 984	0.054 663
MP3	0.074 605	0.073 305	0.072 221	0.073 250
MP4	0.014 860	0.058 582	0.059 170	-0.002 185
MP5	0.016 978	0.002 911	(-0.050 052)	(-0.036 913)
MP6	0.004 058	0.000 173	(-0.003 652 ± 0.072 216 <i>i</i>)	0.000 007

^aReference 32.

^bReference 33.

^cReference 34.

^dReference 35.

^eReference 32, *6s4p1d* basis set.

^fReference 36, *5s3p2d* basis set.

^gReference 32, *5s3p2d* basis set.

TABLE II. Comparison of accuracies of summation approximants, from the results in Table I. The summation methods are partial summation (*S*), rational Padé summation (*R*), unconstrained quadratic summation (*Q_u*), and constrained ($r_0=0$) quadratic summation (*Q_c*). One method is counted as more accurate than another if its summation error is at least 10% less. The entries are the number of systems for which the given relation is true. For example, “*Q_u* > *R, S*” means that *Q_u* is more accurate than *R* and *S*. The numbers in parentheses show the results for the nine class A and the seven class B systems, respectively, considered separately.

	MP2	MP3	MP4	MP5	MP6
<i>Q_u</i> > <i>R, S</i>	0	6 (6,0)	4 (4,0)	12 (6,6)	4 (3,1)
<i>Q_c</i> > <i>R, S</i>	0	0	8 (4,4)	8 (2,6)	8 (3,5)
<i>R</i> > <i>Q_u, S</i>	2 (0,2)	2 (2,0)	2 (2,0)	2 (1,1)	6 (3,3)
<i>R</i> > <i>Q_c, S</i>	2 (0,2)	0	3 (3,0)	2 (1,1)	4 (4,0)
<i>S</i> > <i>Q_u, R</i>	0	0	6 (0,6)	0	3 (1,2)
<i>S</i> > <i>Q_c, R</i>	0	0	2 (0,2)	0	1 (0,1)
<i>Q_u</i> > <i>S</i>	0	9 (8,1)	7 (7,0)	14 (8,6)	7 (5,2)
<i>Q_c</i> > <i>S</i>	0	8 (8,0)	12 (8,4)	13 (7,6)	11 (5,6)
<i>R</i> > <i>S</i>	2 (0,2)	8 (8,0)	8 (8,0)	14 (7,7)	11 (6,5)
<i>Q_u</i> > <i>Q_c</i>	0	7 (6,1)	5 (5,0)	5 (5,0)	5 (4,1)
<i>Q_c</i> > <i>Q_u</i>	16 (9,7)	2 (2,0)	8 (1,7)	6 (2,4)	9 (3,6)

- (c) MP4 and MP5 should be summed with quadratic Padé approximants. For class A systems unconstrained approximants are best while constrained ($r_0=0$) approximants are best for class B systems.
- (d) Class B systems at MP6 should be summed with constrained ($r_0=0$) quadratic approximants.

For class A at MP6 it is best to use one of the Padé methods rather than partial summation, but it is not clear which of the methods will be most reliable.

Table IV, which lists median ratios of errors from the recommended summation methods and from partial summation, gives an indication of how much improvement can be expected. For MP2 the median increase in accuracy from Padé summation is small. However, since the rational approximant $S_{[0/1]} = E_0 / (1 - E_1 / E_0)$ is so easy to compute, and is more accurate than S_1 for all 16 systems in Table I, there is no excuse not to employ it. At higher orders there are occasional cases in which the partial sum is the most accurate result, but the median improvement from the recom-

TABLE III. Energy, in hartree, for $\text{CH}_3^2A_2'$ with $R=2R_e$, from Møller–Plesset perturbation theory with indicated summation method and order. The full CI result is $E_{\text{FCI}} = -39.303\,132$.^a

Order	Partial sum	Rational Padé	Quadratic Padé, unconstrained	Quadratic Padé, $r_0=0$
E_0	-39.123 546	-39.123 546		-39.123 546, 0
MP2	-39.160 114	-39.160 148	-39.123 546	-39.160 080, -0.036 534
MP3	-39.169 229	-39.172 255	-39.200 885, -39.192 912	-39.172 235, -9.739 878
MP4	-39.175 291	-39.187 381	-39.174 843±0.024 181 <i>i</i>	-39.187 831, -39.325 617
MP5	-39.180 360	-39.211 255	-39.173 703±0.023 755 <i>i</i>	-39.185 774, -39.136 261
MP6	-39.185 300	-39.138 368	-39.172 113±0.020 842 <i>i</i>	-39.173 955±0.022 788 <i>i</i>

^aReference 34.

mended summation method can be substantial.

The last column in Table IV addresses the question of whether or not it is worth the effort to proceed to the next higher order of perturbation theory. Alberts and Handy³⁸ have suggested that MP3 does not give sufficient improvement to justify the computational cost. Indeed, for the class B systems considered here the accuracy of MP3 in the median case is lower than that of MP2, even with quadratic summation. For class A systems, however, MP3 does appear to be worth the effort, with median reduction of the error by a factor of 6. Class B systems show substantial improvement at MP4 and MP6. Both classes show only modest improvement at MP5.

The relatively poor accuracy from partial summation is due to the inability of the summation approximants, which are nonsingular at finite z , to model the singularity structure of the energy function $E(z)$ in the complex plane of the perturbation parameter z . The dominant singularity is in general expected to be a two-sheet branch point. The quadratic approximants model this singularity explicitly, with a square-root branch point, but the accuracy of a quadratic approximant can be degraded by a spurious, nonphysical, branch point near z_{phys} . A perusal of the roots of the discriminant polynomial can indicate the likely quality of a particular approximant. Of the systems in Table I, the one with

TABLE IV. Median ratios of errors from summation approximants. $\Delta S_n = S_n - E_{\text{FCI}}$ and $\Delta X_n = X_n - E_{\text{FCI}}$, where $n=1$ for MP2, $n=2$ for MP3, etc., S_n is the partial summation approximant, and X_n is the recommended kind of approximant. The recommended approximants are rational Padé at MP2, constrained ($r_0=0$) quadratic for class B systems at MP4, MP5, and MP6, and unconstrained quadratic otherwise. The entries are the median values for the nine class A systems or for the seven class B systems included in Table I.

Class	Order	$\left \frac{\Delta S_2}{\Delta S_n} \right $	$\left \frac{\Delta S_2}{\Delta X_n} \right $	$\left \frac{\Delta S_n}{\Delta X_n} \right $	$\left \frac{\Delta X_{n-1}}{\Delta X_n} \right $
A	MP2	1	1.01	1.01	4.58
	MP3	2.93	6.08	1.99	6.02
	MP4	6.24	46.2	3.96	2.65
	MP5	11.39	82.5	2.65	1.46
	MP6	24.17	147	3.23	2.33
	B	MP2	1	1.04	1.04
MP3		0.89	0.89	1.03	0.87
MP4		5.89	24.56	1.66	12.9
MP5		4.63	11.4	2.34	1.62
MP6		21.3	2000	3.61	30

branch point closest to z_{phys} for MP6 in the $r_0=0$ approximant is $\text{CH}_2^1A_1$, with branch point at $0.832 \pm 0.018 i$. The accuracy in this case is relatively poor. The same is true at MP5 for H_2O with $R=2R_e$, in which case there is a branch point at 1.11. It is not always clear at low orders whether or not a branch point is spurious. Therefore, unless one suspects on physical grounds that there should be a branch point close to z_{phys} , a quadratic approximant with a singularity near z_{phys} should be treated with suspicion. In the present study the value of r_0 , when treated as a parameter, was chosen as zero. However, it may be feasible to shift spurious branch points away from z_{phys} by varying the value of r_0 .

Perhaps the most striking result described here is that for CH_3 with $R=2R_e$, which is predicted to be a resonance in the ionization continuum. In such cases MPPT could be *more* accurate than a full configuration-interaction calculation. If the basis set consists only of bound-state eigenfunctions, the CI wave function will always correspond to a bound state and this will always lead to a real, and incorrect, result for a resonance energy. The calculation of large-order Møller–Plesset expansions in the course of a CI calculation^{4,10,11} was developed as a method for studying the large-order behavior of the expansion coefficients. However, such expansions, summed with quadratic approximants, could have practical utility as a means for obtaining highly accurate energies and widths of autoionizing resonances.

Quadratic approximants may also prove useful for treating resonances between *bound* states involved in avoided crossings. As the potential energy curves approach each other, a pair of branch points of $E(z)$ at complex-conjugate values of z comes close to z_{phys} . These singularities seriously degrade the convergence of partial sums³⁹ but will have less of an effect on the convergence of quadratic approximants. This is closely analogous to a recent application of quadratic and cubic approximants to resonances between nearly degenerate molecular vibration eigenstates.²³

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