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Summation approximants improve the accuracy of ab initio calculations of molecular potential-energy hypersurfaces

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Abstract

Full configuration–interaction calculations for BH, HF, and CH_3 are used as benchmarks for determining the accuracy of summation approximants for CCSD(T) coupled-cluster theory and fourth-order Møller–Plesset perturbation theory as function of bond distances. A continued-fraction approximant [the CCSD(T)-cf method] reliably improves CCSD(T). The MP4-qλ procedure, in which repartitioned perturbation theory is summed with a quadratic approximant, is much more accurate than conventional MP4 but more sensitive to bond stretching than is CCSD(T)-cf. Diagnostics for estimating the accuracies of the methods, based on singularity analysis of perturbation series, are developed and discussed.

1. Introduction

Ab initio methods with a high-level treatment of electron correlation, having a computational cost scaling proportional to N^7 where N is a measure of the size of the system, fill an important niche in the collection of quantum chemistry tools. The cost is low enough that with present-day computational resources it is feasible to use these methods with large basis sets to accurately characterize the chemistry and spectroscopy of small molecules [1]. The principal N^7 methods are MP4 (fourth-order Møller–Plesset perturbation theory) [2] and

CCSD(T) (coupled-cluster theory with single and double excitations and noniterative treatment of triple excitations) [3]. These are the focus of the present study.

The popularity of MP4 has been waning, in favor of CCSD(T), on account of problems that have been encountered with the convergence of the perturbation series [4–9]. These problems become especially severe as bonds are stretched. However, two recent developments make it necessary to re-evaluate this situation. First, a summation procedure for MP4 has been devised that significantly improves the accuracy obtainable from the perturbation theory [10]. This approach, the MP4-qλ method, involves summing the perturbation series with a quadratic approximant and repartitioning the Hamiltonian using the λ transformation

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[11,12]. Comparison with a set of benchmark full configuration–interaction (FCI) energies showed that this procedure reduced the difference between the MP4 and FCI energies by an order of magnitude, making MP4 on average for typical systems more accurate than CCSD(T) [10]. The second development is the discovery of a summation approximant for coupled-cluster theory, in the form of a continued fraction [13]. This 'CCSD(T)-cf' method seems to reasonably dependably extrapolate the sequence SCF, CCSD, CCSD(T) toward the FCI limit, so that the coupled-cluster results become at least comparable in accuracy to the MP4-qλ results and often significantly more accurate.

The MP4-qλ and CCSD(T)-cf studies focused primarily on atoms and on molecules at their equilibrium geometries. The CCSD(T)-cf study, however, did include an analysis of the calculations by Olsen et al. [7] for the water molecule with the geometry distorted along the symmetric stretch. This analysis indicated that the CCSD(T)-cf method continued to give excellent results with a moderate amount of stretching. Presented here is a more systematic study of the effects of bond stretching on the accuracy of these methods. We have carried out FCI calculations for the molecules BH, HF, and CH_3 over closely spaced intervals of bond stretching as a benchmark for comparing the MP4, CCSD(T), MP4-qλ, and CCSD(T)-cf methods. Our primary goal is to determine which of these methods would be the best choice for practical applications. We will also examine the way in which the various methods fail in response to the symmetry breaking effects that occur in spin-restricted treatments of homolytic bond cleavage and develop diagnostics for predicting the magnitude of these effects.

2. Methods

The MP4-qλ method is based on functional analysis of the MP energy in the complex plane of the perturbation parameter. The Møller–Plesset partitioning of the Hamiltonian is [2]

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

where H_{phys} is the physical Hamiltonian and H_0 is the sum of one-electron Fock operators. This construction introduces the parameter z in order to have an analytic continuation from the Hartree–Fock self-consistent field (SCF) solution at $z = 0$ to the true solution at $z = 1$. The energy is obtained as a power series, $E(z) \sim E_0 + E_1 z + E_2 z^2 + \cdots$, which is the unique asymptotic expansion of a function $E(z)$. The zeroth-order approximation, E_0, is the sum of one-electron orbital energies. The Hartree–Fock approximation for the total energy is $E_{\text{SCF}} = E_0 + E_1$.

The conventional approach to MP4 is simply to add up the truncated power series, in terms of the 'partial summation' approximant

$$S_n(z) = \sum_{i=0}^{n} E_i z^i. \qquad (2)$$

The usual MP4 result is $S_4(1)$. However, the true functional form of $E(z)$ is multiple valued, with branch-point singularities that can strongly affect the convergence of Eq. (2) [14–18].

The qλ method uses a quadratic summation approximant,

$$S_{[L/M,N]}(z) = \frac{1}{2}\frac{P_L}{Q_M} \pm \frac{1}{2Q_M}\sqrt{P_L^2 - 4Q_M R_N}, \qquad (3)$$

to explicitly model the most important branch point. P_L, Q_M, and R_N are polynomials in z of degrees L, M, N, respectively, such that the Taylor series of $S_{[L/M,N]}$ agrees with the perturbation series of E up to the desired order. The effectiveness of quadratic approximants for MP4 is improved by using them in conjunction with Hamiltonian repartitioning. The idea is to define a new partitioning of the operator $H(z)$ so that the energy function $E(z)$ has a singularity structure in the complex z plane that is more amenable to summation. This is accomplished by changing the way in which the Hamiltonian is divided between the operators H_0 and H_1. One way to do this is the Feenberg repartitioning [11],

$$H^{(\lambda)}(z) = \frac{1}{1-\lambda}H_0 + z\left(H_1 - \frac{\lambda}{1-\lambda}H_0\right), \qquad (4)$$

where λ is an arbitrary parameter. At the physical point $z = 1$ Eq. (4) yields H_{phys}, but elsewhere in

the z plane different values of λ give a different Hamiltonian. An advantage of this particular repartitioning is that the perturbation series coefficients for arbitrary λ can be expressed as a linear combination of the $\lambda = 0$ series coefficients [12],

$$E_i^{(\lambda)} = \sum_{k=1}^{i-1} \binom{i-2}{k-1} \lambda^{i-k-1} (1-\lambda)^k E_{k+1} \qquad (5)$$

for $i \geqslant 2$, with the Hartree–Fock energy, $E_{SCF} = E_0 + E_1$, left unchanged. As implemented in [10], the quadratic approximant is applied to a series $\tilde{E}_0 + \tilde{E}_1 z + \tilde{E}_2 z^2 + \tilde{E}_3 z^3$ where $\tilde{E}_0 = E_{SCF}$ and $\tilde{E}_i = E_{i+1}$ for $i \geqslant 1$.

MP series can be grouped into two classes according to their large-order behaviors [12,19–21]. Class-A series characteristically have E_i mostly of the same sign while class-B series have E_i that alternate in sign. These behaviors depend in principle on the location of the dominant singularity z_d, which is the singularity of $E(z)$ closest to the origin of the z plane. If z_d is in the positive half plane then class-A behavior is expected and if it is in the negative half plane then class B is expected. The MP class of a given system can be predicted in advance from the qualitative nature of the orbital structure according to criteria developed by Cremer and He [21]. Systems with crowded orbitals, such as closed-shell systems with highly electronegative atoms or molecules with multiple bonds, are in class B, while radicals and systems such as alkanes with well-separated orbitals are in class A.

The class-A singularity structure typically arises from a near degeneracy between the ground state and the first excited state of the same symmetry. The energy functions for these two states cross at a complex–conjugate pair of branch points with real part greater than 1 and imaginary part close to zero [14,15,18,22]. Class-B singularity structure seems to usually be due to a phase transition at a critical point on the negative z axis, where the ground-state energy function crosses the energy of an autoionizing state [16–18]. The operator H_1, in Eq. (1) contains the interelectron potential energy $1/r_{12}$. When z is negative the interaction between electrons is attractive, and as $|z|$ increases there comes a critical point at which the lowest-energy state of the system corresponds to a bound cluster of electrons dissociated from the nuclei.

The class-A branch points connect states that have almost equal energies at the physical point $z = 1$, while the class-B branch point connects the ground state energy with an energy function that represents a highly excited state at $z = 1$ [6]. In principle [23], the case of the ground state crossing a highly excited state is best described by an approximant with the constraint $r_0 = 0$ on the polynomial $R(z)$. For MP4 the approximant index [1/0,2] is used, because the [1/1,1] approximant gives a result that is independent of λ. The value of λ will be chosen to maximize $|z_d|$ in the negative half plane. This summation method will be designated MP4-q$\lambda^{(-)}$. The case of class-A physically nearly degenerate states is best described with the unconstrained [1/0,1] approximant with λ chosen to maximize $|z_d|$ in the positive half plane. This method will be called MP4-q$\lambda^{(+)}$.

The functional analysis for coupled-cluster theory is less straightforward than that for perturbation theory. However, an empirical analysis of the convergence of the sequence E_{SCF}, E_{CCSD}, $E_{CCSD(T)}$ toward the FCI limit has been carried out [13] and comparison with a benchmark set of FCI energies for a variety of atoms and small molecules indicated that the continued-fraction approximant

$$E_{CCSD(T)cf} = \frac{\delta_1}{1 - (\delta_2/\delta_1)/(1 - \delta_3/\delta_2)}, \qquad (6)$$

where

$$\delta_1 = E_{SCF}, \qquad (7)$$

$$\delta_2 = E_{CCSD} - E_{SCF}, \qquad (8)$$

$$\delta_3 = E_{CCSD(T)} - E_{CCSD}, \qquad (9)$$

significantly improves the accuracy of the total energy, especially for systems with class-A perturbation series.

For the analysis that follows we calculated FCI energies with the MOLPRO 2000 software package, which uses the algorithm of Knowles and Handy [24]. For the closed-shell systems BH and HF the CCSD(T) and MP4 calculations were done with MOLPRO's spin-restricted algorithms [25], and for the open-shell system CH_3 we used MOLPRO's spin-unrestricted UCCSD(T) and partially

spin-restricted RCCSD(T) algorithms [25,26]. MP4 calculations for CH_3 were done with GAUSSIAN 98 [27]. Spin-unrestricted results were obtained from the UMP4 algorithm and spin-restricted results were obtained from the PMP4 spin state projection algorithm [28].

3. Results

Our FCI results are presented in Table 1. The basis set was cc-pVTZ for BH and cc-pVDZ for HF and CH_3. The calculations were carried out at evenly spaced multiples of the equilibrium bond distances, R_e, with the values of R_e for HF and BH taken from FCI calculations [9] and for CH_3 determined from RCCSD(T) calculations. These values were then used with all of the calculation methods, so that comparisons of different methods always use the same molecular geometry.

Fig. 1 compares the accuracy of the various calculation methods as a function of bond distance, R, for the HF molecule. This is a class-B system. The first panel shows the error in the total energy, $E_{approx} - E_{FCI}$, while the second shows the error in the energy relative to the values at $R = R_e$. Since these are spin-restricted calculations with a single reference determinant, they cannot correctly describe the molecule in the dissociation limit [29]. However, the CC methods and the MP4-q$\lambda^{(+)}$ method give good results for total energy up to approximately $2R_e$. For the relative energy, the best results are from MP4-q$\lambda^{(+)}$ up to $1.5R_e$ and then CCSD(T)-cf up to $1.9R_e$. MP4-q$\lambda^{(-)}$ and conventional MP4 work well enough at R_e but their accuracies are very sensitive to the value of R, which leads to poor results for the relative energy.

The two lower panels of Fig. 1 show the error, compared to FCI results, in the gradient, $E' = dE/dr$, $r = R/R_e$, and in the second derivative,

Table 1
Full configuration–interaction energies in units of E_h for hydrogen fluoride, boron hydride, and the methyl radical as a function of bond distance, R

R/R_e [a]	$^1\Sigma^+$ HF	$^1\Sigma^+$ BH	$^2A_2''$ CH_3
0.90	−100.21671960	−25.22456740	−39.67784787
0.95			−39.70568869
1.00	−100.22865236	−25.23113558	−39.71632504
1.05			−39.71421359
1.10	−100.22110308	−25.22686904	−39.70277149
1.15			−39.68462676
1.20	−100.20401683	−25.21708645	−39.66180734
1.25			−39.63588366
1.30	−100.18283498	−25.20479316	−39.60807607
1.35			−39.57933582
1.40	−100.16062248	−25.19169500	−39.55040586
1.45			−39.52186687
1.50	−100.13913011	−25.17875751	−39.49417235
1.55			−39.46767546
1.60	−100.11932658	−25.16651594	
1.70	−100.10169672	−25.15525860	
1.80	−100.08642887	−25.14513621	
1.90	−100.07353095	−25.13622036	
2.00	−100.06289468	−25.12852903	
2.10	−100.05432915	−25.12203546	
2.20	−100.04758473	−25.11667257	
2.30	−100.04237901		
2.40	−100.03842539		
2.50	−100.03545825		

[a] R_e is the equilibrium bond distance. The values used are 0.920250, 1.235602, and 1.078813 Å, respectively, for HF, BH, and trigonal planar CH_3.
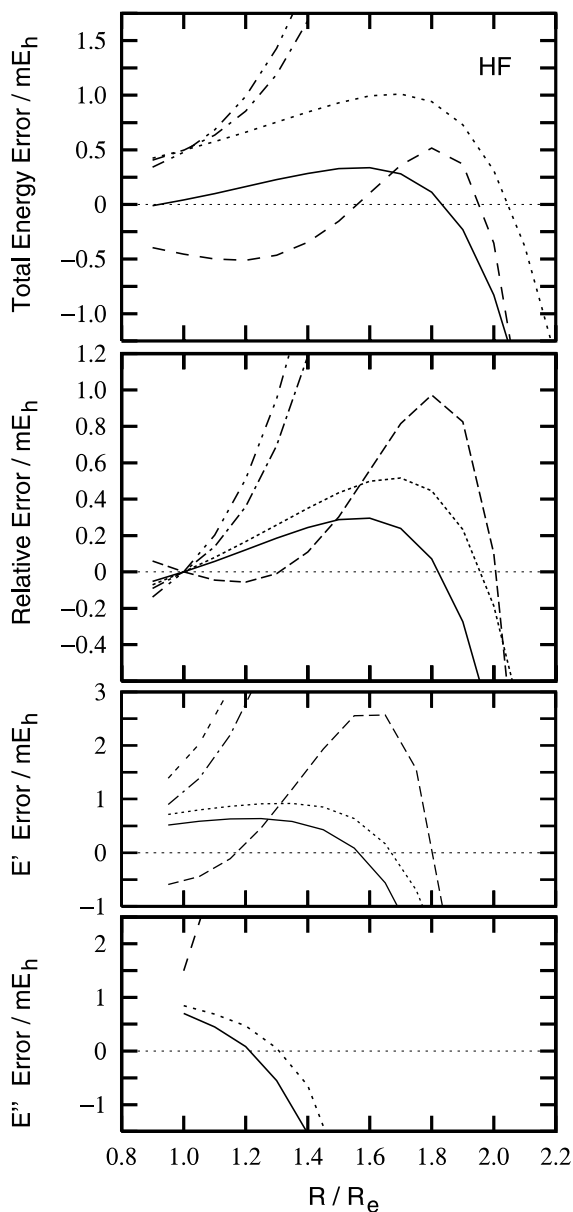
Fig. 1. Accuracy of energy approximant as function of bond distance for the hydrogen fluoride molecule. The calculation methods are conventional CCSD(T) (dotted curve), CCSD(T)-cf (solid curve), conventional MP4 (dash–dot curve), MP4-q$\lambda^{(-)}$ (dash–dot–dot curve) and MP4-q$\lambda^{(+)}$ (dashed curve). The total energy error is $E_{\mathrm{approx}} - E_{\mathrm{FCI}}$. The relative energy error is $\Delta E_{\mathrm{approx}} - \Delta E_{\mathrm{FCI}}$, where $\Delta E = E(R) - E(R_{\mathrm{e}})$. The E' error is $E'_{\mathrm{approx}} - E'_{\mathrm{FCI}}$, where $E' = \mathrm{d}E/\mathrm{d}r$, $r = R/R_{\mathrm{e}}$. The E'' error is $E''_{\mathrm{approx}} - E''_{\mathrm{FCI}}$, where $E'' = \mathrm{d}E'/\mathrm{d}r$.
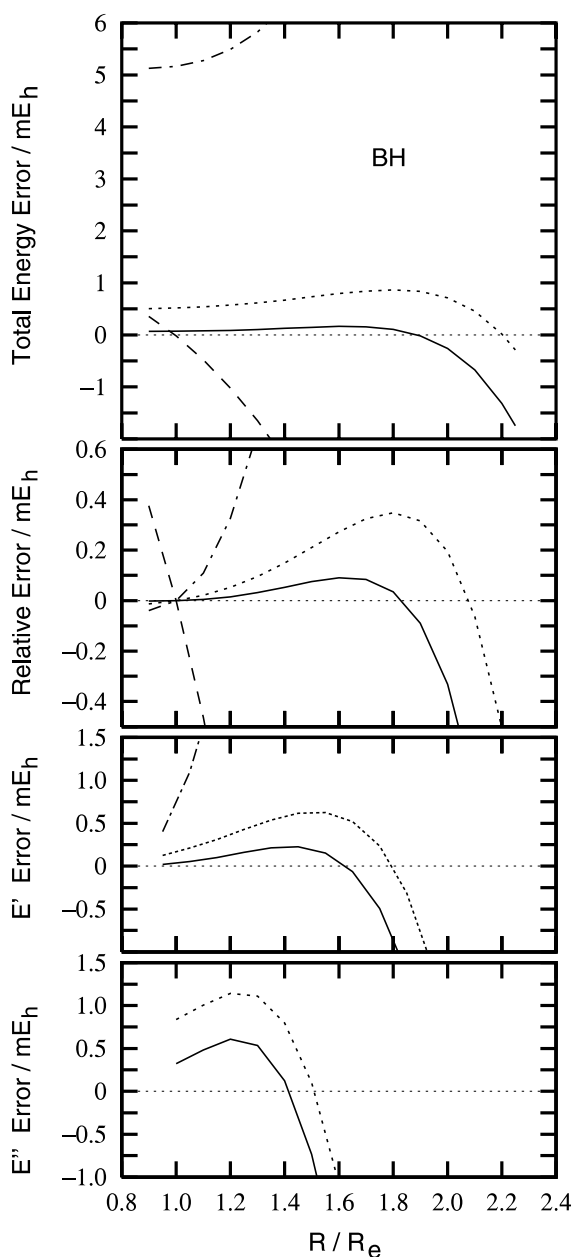
Fig. 2. Accuracy of energy approximant as function of bond distance for the BH molecule. The calculation methods are conventional CCSD(T) (dotted curve), CCSD(T)-cf (solid curve), conventional MP4 (dash–dot curve), and MP4-q$\lambda^{(+)}$ (dashed curve). The y axes are defined as in Fig. 1.

$E'' = \mathrm{d}^2 E/\mathrm{d}r^2$. These values were calculated from finite differences of the energy values. The best results for E' are from MP4-q$\lambda^{(+)}$ up to about $1.3R_{\mathrm{e}}$ and from CCSD(T)-cf between 1.3 and $1.6R_{\mathrm{e}}$. However, both of the CC methods give better results for E'' than does MP4-q$\lambda^{(+)}$, and CCSD(T)-cf is better than conventional CCSD(T).

Fig. 2 shows results for the boron hydride molecule, a class-A system. Here the CCSD(T)-cf method is remarkably accurate, for the energy and for the derivatives. The total energy error is on the order of 0.1 mE_{h} for R up to $1.9R_{\mathrm{e}}$. All of the MP4 methods work poorly for this system. Although the q$\lambda^{(+)}$ summation method significantly reduces the MP4 error in the total energy, its accuracy shows a strong sensitivity to the value of R, and its results for E' and E'' are not good. CCSD(T)-cf gives excellent accuracy for E' and E'' (in the region before the dissociation failure sets in) and is a significant improvement over CCSD(T).

In Fig. 3 we present results for the ground state of the methyl radical, an open-shell system. The curves are labeled 'r' or 'u' to indicate that the calculations are spin-restricted or spin-unrestricted, respectively. R is the C–H bond distance for a trigonal planar symmetric stretch. The cf approximant improves the accuracy of both the total and relative CCSD(T) energies. The qλ approximant greatly improves the UMP4 accuracy of the total energy and, in contrast to the case of BH, also improves the accuracy of the relative energy, so much so that UMP4-qλ here gives the most accurate relative potential-energy curve up to about $1.4R_{\mathrm{e}}$, after which it fails quite rapidly. In the vicinity of the equilibrium geometry, UMP4-qλ gives about the same accuracy as CCSD(T)-cf for E' and E''. We also considered the spin-restricted PMP4 method [27,28]. (The results are not included in Fig. 3.) The conventional PMP4 results are slightly better than the conventional UMP4 results, but PMP4-qλ is much less accurate than UMP4-qλ.

4. Discussion

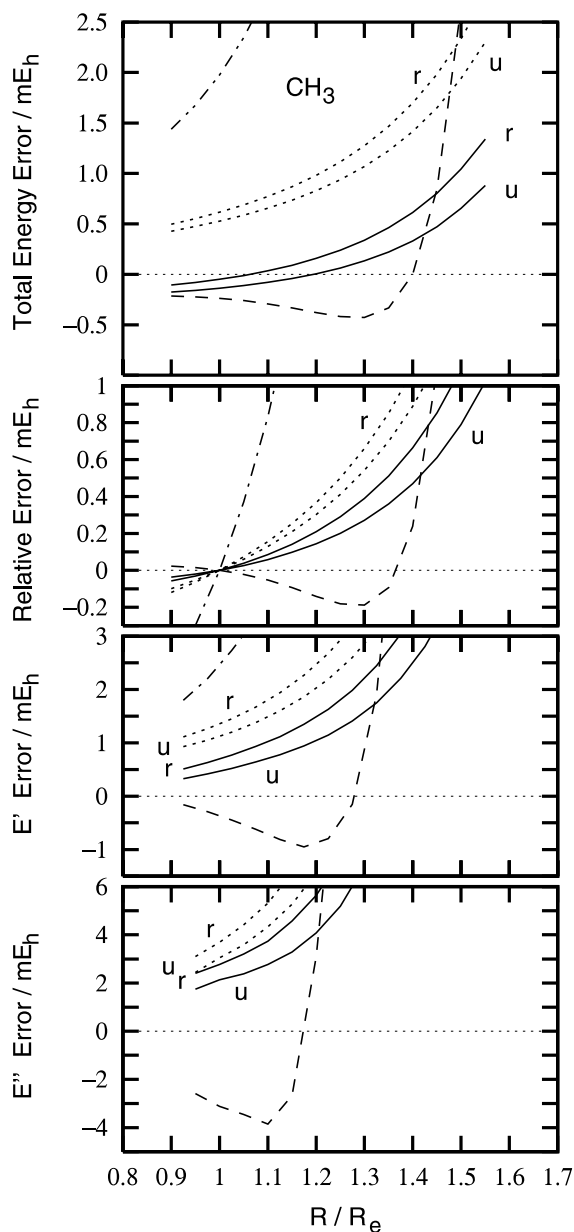We have considered here a representative sample of molecule types (the class-B system HF, the

Fig. 3. Accuracy of energy approximant as function of bond distance for the CH_3 molecule. The calculation methods are conventional CCSD(T) (dotted curve), CCSD(T)-cf (solid curve), conventional UMP4 (dash–dot curve), and UMP4-q$\lambda^{(+)}$ (dashed curve). The coupled-cluster curves are labeled 'r' for spin-restricted calculations and 'u' for spin-unrestricted calculations. The y axes are defined as in Fig. 1.

closed-shell class-A system BH, and the open-shell class-A system CH_3) and have found that in all of these cases the CCSD(T)-cf method, proposed in [13], gives more accurate results than conventional CCSD(T) for total energies and relative energies as bond lengths are stretched, and for energy derivatives. This is consistent with previous tests of the method for a large variety of small atoms and molecules at their equilibrium geometries [13]. Once one has computed the SCF, CCSD, and conventional CCSD(T) energies, the CCSD(T)-cf energy is trivial to calculate, according to Eq. (6). Therefore, this is an easy way to significantly increase the accuracy of ab initio results with high-level electron correlation, and it can be readily implemented using output from standard software packages.

Figs. 1–3 show that MP4-qλ is sometimes more accurate than CCSD(T)-cf but often is considerably less accurate. This can be understood in terms of the singularity structure of $E(z)$. Fig. 4 shows the position z_d of the dominant singularity of the MP4-q$\lambda^{(+)}$ approximant as a function of R. This is a square-root branch point, connecting Riemann sheets corresponding to the ground state and the first excited state of the same symmetry. (In principle, there is a complex–conjugate pair of branch points slightly displaced from the real axis, but at fourth order the approximant models these with a single branch point on the real axis.) For calculations based on a single spin-restricted Hartree–Fock reference state, these two eigenstates become degenerate in the limit of large R. As R increases, z_d approaches the physical point $z = 1$, which is where the approximant is to be evaluated. This means that a small inaccuracy in the description of the branch point will cause a relatively large error in the energy value.

In previous studies [10,13] it was found that the q$\lambda^{(-)}$ summation approximant was the appropriate MP4 approximant for calculating total energies of class-B atoms and of class-B molecules at equilibrium geometries. Here, however, we find that for the HF molecule the q$\lambda^{(-)}$ approximant is quite sensitive to distortions of the molecular geometry and therefore gives poor results for the potential-energy curve while the q$\lambda^{(+)}$ approximant gives excellent results up to about 1.5 R_e. The
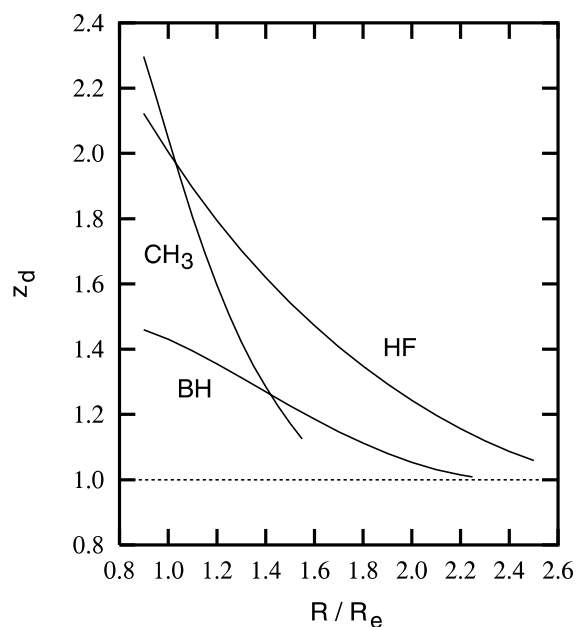

Fig. 4. Position of dominant singularity z_d in the MP4-q$\lambda^{(+)}$ quadratic approximant for BH, HF, and CH_3, with the repartitioning parameter chosen to maximize $|z_d|$ in the positive half plane.

q$\lambda^{(+)}$ approximant was originally developed as an approximant for class-A systems, and in practice gave on average slightly less accurate results for total energies of class-B systems than did q$\lambda^{(-)}$ in the previous studies. As R increases, the relative energy accuracy is affected by the singularity structure in the positive half plane, which is shifting. The singularity structure in the negative half plane can depend on the choice of basis set [10,13], but is apparently not as sensitive to the molecular geometry. This would explain why better results for the shape of the potential-energy curve are obtained from the approximant that models the singularity structure in the positive half plane than from the approximant that models the structure in the negative half plane.

At fourth order in perturbation theory the branch point location is not yet fully converged, and the closer the branch point is to the point $z = 1$ the more important it is to describe it precisely. This effect is illustrated by Fig. 5, which shows the error in the MP4-q$\lambda^{(+)}$ value for the
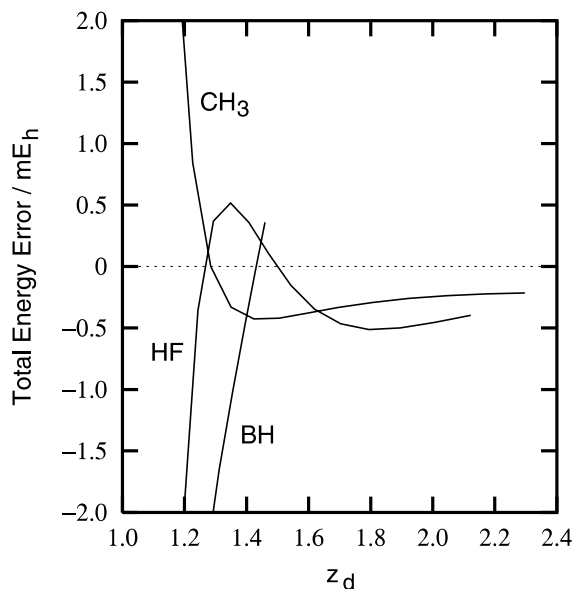
Fig. 5. Accuracy of the MP4-q$\lambda^{(+)}$ approximant for total energy as function of the position of the dominant singularity of the approximant.

energy as a function of z_d. The energy values are unreliable when z_d is less than about 1.6. Thus, the value of z_d provides a diagnostic of the accuracy of the MP4-q$\lambda^{(+)}$ approximant, indicating the region of the potential-energy hypersurface in which the results of the calculation will be dependable. For BH, z_d is less than 1.6 over the full range of R. This is presumably related to the small HOMO–LUMO gap for this molecule [8]. The extremely accurate MP4-q$\lambda^{(+)}$ result for the energy at R_e would appear to be fortuitous. For the other two molecules there are significant regions, in Figs. 1 and 3, with $z_d > 1.6$, and throughout these regions MP4-q$\lambda^{(+)}$ gives a smaller error in the relative energy curve than do the coupled-cluster methods.

The results presented here and in [13] demonstrate that the continued-fraction approximant can significantly improve the accuracy of the CCSD(T) method. Nevertheless, the justification for this approximant is essentially empirical. The functional analysis of CC theory is more complicated than that for perturbation theory. Although the CC method is usually formulated as a rearrangement of the configuration–interaction expansion, it is possible to formulate the CC expression for the energy in terms of the MP energy series [30]. The CCSD truncation contains all the terms that make up the MP3 partial sum plus additional terms that appear only at higher order in the MP series. The CCSDT truncation contains all the terms in the MP5 partial sum plus higher-order terms. However, on account of the presence of incomplete higher-order contributions, the CC energy expressions are not asymptotic series. A further complication comes from the use of the CCSD(T) approximation to the full CCSDT energy. Stanton [31] has shown that a similar approximation can be expressed in the form of a series expansion. The Hamiltonian is partitioned as an infinite series of operators that leads to a perturbation series for E such that truncation at third-order yields an expression similar to the CCSD(T) energy [32]. In principle, a singularity analysis of this series could lead to a theoretically derived summation approximant. However, summation of the series $\delta_1 + z\delta_2 + z^2\delta_3$ with a quadratic approximant, which would be perhaps the simplest way to accomplish this, in practice gives less accurate results than the continued fraction [13].

All of the methods considered here fail as bonds are stretched toward dissociation. For the MP4 methods, this can be explained in terms of the position of the dominant branch point. CCSD(T) is more resistant to this effect, but it too eventually fails, presumably because of the fact that the MP4 wavefunction is used to calculate the (T) correction. [CCSD(T) fails somewhat earlier than CCSD and CCSDT, which do not rely on MP calculations.] The CCSD(T)-cf curves in Figs. 1 and 2 fail slightly earlier than do the CCSD(T) curves, but this is probably due to cancellation of errors. The CCSD(T) results are initially too high but in the dissociation limit the energy plunges below the correct value.

For the molecules considered here, CCSD(T)-cf continues to be accurate up to at least $1.5R_e$. Therefore, the method can be expected to be adequate for describing transition states, which typically involve geometry distortions no more severe than this. Multireference methods are probably necessary for describing the process of molecular dissociation, but on account of the relatively

greater expense of such a calculation, it would be useful to have a diagnostic that would indicate how long it is safe to continue to use single-reference CCSD(T)-cf. Such a diagnostic, for class-B systems, was suggested in [13], based on the singularity structure of the MP energy function in the *negative* half plane. It was noted that the CCSD(T)-cf total energy error exceeded 1 mE_h if the nearest branch point in the MP4-q$\lambda^{(-)}$ approximant on the negative z axis lay closer to the origin than approximately −1.2. For the HF molecule, we find that this branch point starts at −2.7 for $R = R_e$ and steadily approaches the origin as R increases, passing through −1.2 at $2.05R_e$. The top panel of Fig. 1 shows that the magnitude of the cf error rises above 1 mE_h at $2.02R_e$, in remarkable agreement with the diagnostic. We have not yet identified a comparably successful diagnostic for class-A systems.

The results for energy derivatives in Figs. 1–3 were calculated from finite differences using the spacing of R values in Table 1. This spacing is too coarse to give quantitative values for molecular properties such as vibrational frequencies, but it is good enough to indicate the trends in the accuracies of the various methods. The cf approximant consistently improves the accuracies not just of E but also of E' and E''. This means that the amount by which the approximant lowers the CCSD(T) value varies correctly with R, which suggests that the approximant is actually modeling the underlying convergence pattern of the theory. The results for the MP4-qλ derivatives emphasize the sensitivity of that method to the position of the branch points. The advantage of such sensitivity is that if the branch-point diagnostic is favorable then one can have added confidence in the accuracy of the results. The disadvantage is that, at least for the cases considered here, the diagnostic is often unfavorable.

The cf and qλ methods can both be used with analytical values of energy derivatives. For the cf method, one could simply differentiate Eq. (6) with respect to R and then substitute the analytical values of the SCF, CCSD, and CCSD(T) derivatives into the resulting expression. Alternatively, it might be possible to find an approximant that directly extrapolates the sequence E'_{SCF}, E'_{CCSD},

$E'_{CCSD(T)}$. For MP4, the best approach is probably to apply the qλ summation procedure to the asymptotic series of the derivative,

$$E'(z) \sim E'_{SCF} + E'_{MP2}z + E'_{MP3}z^2 + E'_{MP4}z^3. \qquad (10)$$

If $E(z)$ has a branch point at a point z_d, then $E'(z)$ will also have a branch point at z_d. Therefore, the same summation procedure ought to work for either function.

Acknowledgements

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