Regular article

Maximum radius of convergence perturbation theory: test calculations on Be, Ne, H₂ and HF

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Abstract. Maximum radius of convergence (MAXR_c) perturbation theory [(2000) *Journal of Chemical Physics* 112:6997] is tested on the beryllium and neon atoms using calculations that are truncated in high orders. Calculations are also performed on the ground-state potential-energy curves of H₂ and HF. The neon atom calculations use the 3-21G basis set with added diffuse *s* and *p* functions. All other calculations use the STO-3G minimum basis set. MAXR_c perturbation theory consistently performs well. The Epstein–Nesbet and Møller–Plesset perturbative expansions frequently diverge or exhibit slow convergence compared to the expansions obtained from MAXR_c.

Keywords: Maximum radius – Perturbation theory – Convergence

1 Introduction

One of the most successful ab initio approaches is Møller–Plesset (MP) perturbation theory, especially when truncated after the second order [1, 2, 3]. Unfortunately, partitioning is not always effective beyond the second order, where damping and divergent behavior may appear [4, 5]. Recently, we have developed a new approach called maximum radius of convergence (MAXR_c) perturbation theory that is an alternative to the MP and Epstein–Nesbet (EN) [6] partitionings. This method will – hopefully – deliver better convergence than traditional approaches. The MAXR_c approach is based on choosing the energy denominators in a Rayleigh–Schrödinger perturbation expansion in a manner that is (approximately) "optimal". We test the MAXR_c perturbation theory on the ground states of the beryllium and neon atoms using

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calculations that are truncated in high orders in Sect. 3. High-order calculations are also performed on the ground-state potential-energy curves of H₂ and HF. Before presenting the results, we briefly review the MAXR_c method.

2 MaxR_c theory

Consider a two-state system consisting of a single reference state, denoted by $|p\rangle$, and a single orthogonal space state, denoted by $|q\rangle$. Let E_p^0 and E_q^0 be their zeroth-order energies that define a diagonal, zeroth-order Hamiltonian,

$$H_0 = |p\rangle E_p^0 \langle p| + |q\rangle E_q^0 \langle q| \ . \tag{2.1}$$

The radius of convergence R_c for the two-state Rayleigh–Schrödinger perturbation expansion is easily derived [7],

$$R_c^2 = \frac{\Delta E^2}{(\Delta E - H_p^q)^2 + 4|\langle p|H|q\rangle|^2} \ , \tag{2.2}$$

where

$$H_p^q = \langle p|H|p\rangle - \langle q|H|q\rangle \ , \tag{2.3}$$

and ΔE is the sole energy-denominator factor appearing in the perturbation expansion,

$$\Delta E = E_p^0 - E_q^0 \ . \tag{2.4}$$

The perturbation expansion is convergent if $R_c \geq 1$, and divergent if $0 \leq R_c < 1$ (note that $R_c \geq 0$). Since H_0 is arbitrary, ΔE is at our disposal. The value of ΔE that yields the maximum radius of convergence is given by [8]

$$\Delta E_m^{(pq)} = H_p^q + \frac{4|\langle p|H|q\rangle|^2}{H_p^q} \ . \tag{2.5}$$

Now consider an N-state system involving one reference states $|p\rangle$ and many orthogonal space states: $|q\rangle$, $|q'\rangle$, $|q''\rangle$, …. The Rayleigh–Schrödinger perturbative expansion for the correlation energy, E_{corr}, is given by

$$E_{corr} = \sum_q \frac{\langle p|V|q\rangle\langle q|V|p\rangle}{E_p^0 - E_q^0}$$

$$+ \sum_q \left[\sum_{q'} \frac{\langle p|V|q\rangle\langle q|V|q'\rangle\langle q'|V|p\rangle}{(E_p^0 - E_q^0)(E_p^0 - E_{q'}^0)} \right.$$

$$\left. - \frac{\langle p|V|q\rangle\langle q|V|p\rangle\langle p|V|p\rangle}{(E_p^0 - E_q^0)^2} \right] + \cdots, \qquad (2.6)$$

where the perturbation, V, is given by $(V = H - H_0)$, and it is determined by H_0:

$$H_0 = |p\rangle E_p^0 \langle p| + \sum_q |q\rangle E_q^0 \langle q| . \qquad (2.7)$$

MAXR_c perturbation theory makes the following choices:

$$E_p^0 = \langle p|H|p\rangle \qquad (2.8)$$

and

$$E_q^0 = \langle q|H|q\rangle - \frac{4|\langle p|H|q\rangle|^2}{H_p^q} . \qquad (2.9)$$

Therefore, the energy denominators for MAXR_c are given by

$$E_p^0 - E_q^0 = \Delta E_m^{(pq)} , \qquad (2.10)$$

and Eq. (2.6) becomes

$$E_{corr} = \sum_q \frac{\langle p|V|q\rangle\langle q|V|p\rangle}{\Delta E_m^{(pq)}}$$

$$+ \sum_q \left[\sum_{q'} \frac{\langle p|V|q\rangle\langle q|V|q'\rangle\langle q'|V|p\rangle}{\Delta E_m^{(pq)} \Delta E_m^{(pq')}} \right.$$

$$\left. - \frac{\langle p|V|q\rangle\langle q|V|p\rangle\langle p|V|p\rangle}{\left(\Delta E_m^{(pq)}\right)^2} \right] + \cdots . \qquad (2.11)$$

A MAXR_c spin-adapted formalism is also available [8] that preserves the linked diagram theorem by using Rayleigh–Schrödinger perturbation theory with flexible energy denominators [9].

3 Results: calculations on Be, Ne, H₂ and HF

Perturbation calculations were performed with the EN, MP, and MAXR_c perturbative methods on Be, Ne, H₂ and HF, using canonical Hartree–Fock orbitals and a configuration state function basis. The α- and β-spin orbitals are restricted — they have a common spatial part. The Ne calculations use the 3-21G basis set [10] with two diffuse s functions (exponents 0.1379 and 0.03137) and a set of diffuse p functions (exponent 0.1379). All other calculations use the STO-3G minimum basis set [10]. For our purposes, calculations are considered to be convergent when estimates of the full configuration interaction (FCI) improve as the order of the perturbation increases. However, it is possible, that divergence can still appear beyond the truncation order.

The order-by-order results for Be using the MP, EN, and MAXR_c partitioning methods up to the tenth order $(N = 10)$ are presented in Fig. 1. The energy axis corresponds to $(E_N - E_\infty)$, where E_N is the Nth-order energy and E_∞ is the infinite-order result obtained from the FCI. EN exhibits slower convergence then the other two methods. MP and MAXR_c exhibit similar behavior, except for the second order where MAXR_c is better. We have also performed higher-order calculations $(10 < N < 100)$ and found nothing unusual – all three methods appear to converge.

The order-by-order results for Ne up to the tenth order $(N = 10)$ are presented in Fig. 2. All methods yield similar results with only small deviations: MP is a little better from $N = 3$ to $N = 6$, but worse at $N = 2$. We have also performed higher-order calculations $(10 < N < 100)$. Both EN and MAXR_c (apparently)
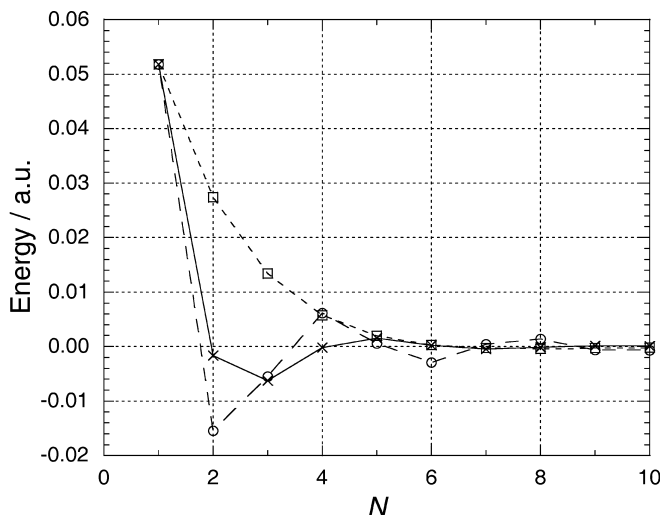
Fig. 1. The beryllium atom computed using Møller–Plesset (MP) (*squares*), Epstein–Nesbet (EN) (*circles*), and maximum radius of convergence (*MAXR_c*) (*crosses*) partitioning methods up the tenth order $(N = 10)$. The energy axis corresponds to $(E_N - E_\infty)$, where E_N is the Nth-order energy and E_∞ is the infinite-order result obtained from the full configuration interaction *FCI*
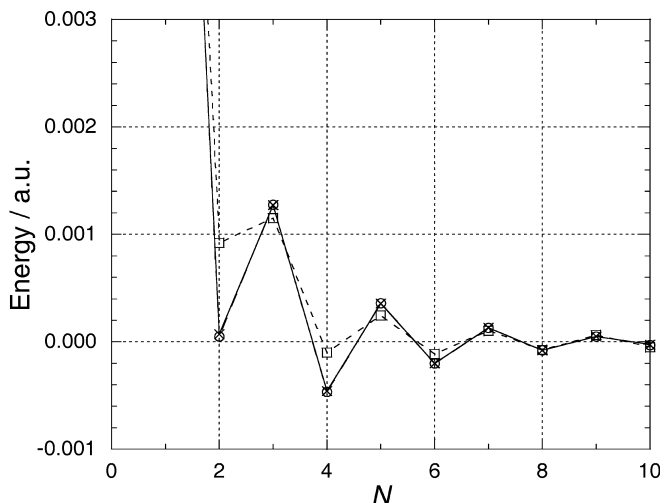
Fig. 2. Same as Fig. 1, but for neon

converge, but MP diverges. The high-order (oscillatory) divergent behavior for MP is given Fig. 3. Similar MP results using diffuse basis sets for Ne have been previously discovered by Olsen and coworkers [4, 5].

The potential-energy curve for H_2 computed through the 200th order ($N = 200$) is presented in Fig. 4. All methods converge in the well region. EN diverges for all geometries greater than about 1.4 Å. MP diverges for geometries greater than about 2.0 Å. The approximate onsets of divergence for both curves are indicated by lines parallel to the energy axis (labeled by EN and MP). MAXR_c exhibits no divergence behavior over the entire range of the potential curve. However, as anticipated, the convergence becomes very slow at large bond distances w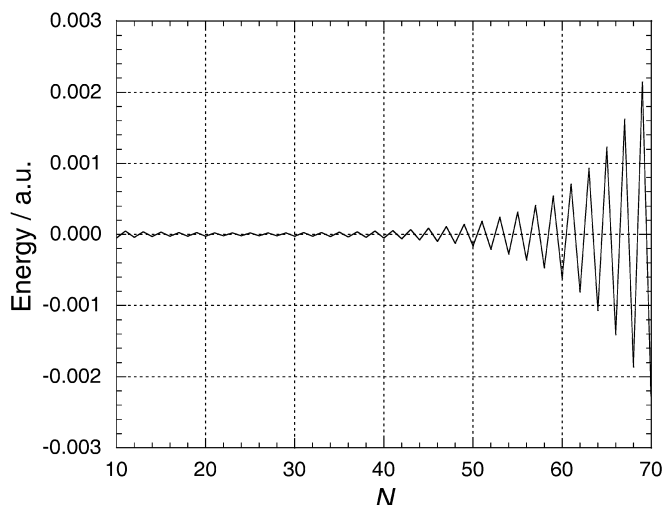here the closed-shell reference state cannot describe the system. At the dissociation limit the reference state becomes degenerate in first order with the (single) orthogonal state, making the energy denominator infinite for MAXR_c. Slow convergence behavior is evident between 3.2 and 4.0 Å where the agreement between MAXR_c and the FCI is poor.

The solid line in Fig. 5 presents the weight ($|C_{ref}|^2$) of the reference determinant for the (two-dimensional) FCI wavefunction of H_2 over the range of internuclear distances considered. Note that the onset of the divergent behavior for EN and MP – indicated by ○ and □ in the figure – corresponds to weights of 0.90 and 0.71, respectively. The weight is 0.5 at the dissociation limit.

Fig. 3. Same as Fig. 2, but between ($N = 10$) and ($N = 70$) and only for MP partitioning

Fig. 5. The weight ($|C_{ref}|^2$) of the reference determinant for the FCI wavefunction of H_2 (*solid line*) and HF (*dashed line*) over the range on internuclear distances considered. The points where divergence first appears for MP (*squares*) and EN (*circles*) partitionings are indicated by *filled* and *unfilled* symbols for H_2 and HF, respectively
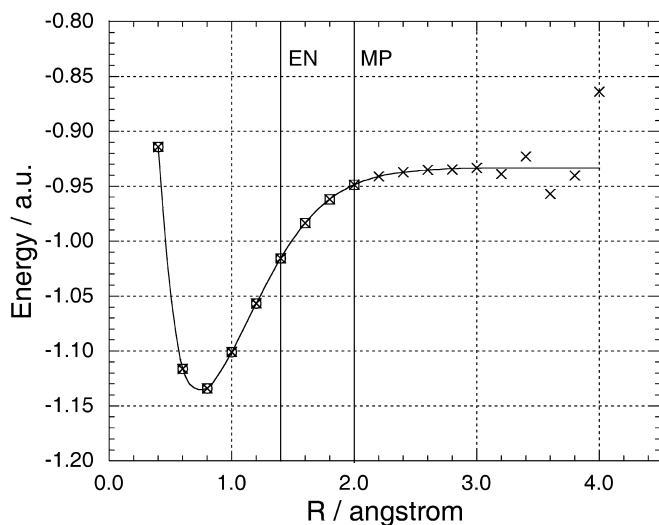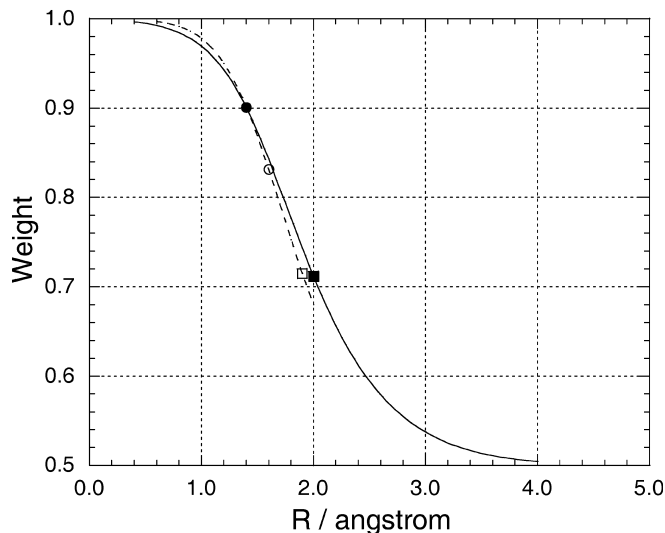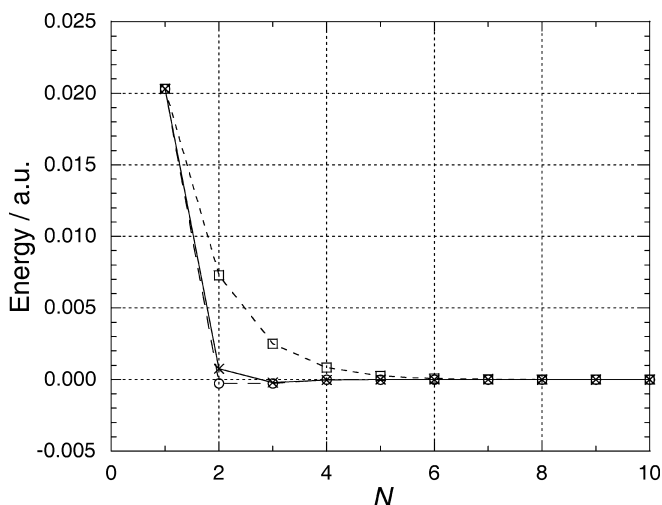

Fig. 4. The potential energy curve of H_2 computed using the MP (*squares*), EN (*circles*), and MAXR_c (*crosses*) partitioning methods for $N = 200$. The *solid line* denotes the exact FCI curve. EN and MP partitioning methods yield divergent expansions for internuclear distances, R, greater than about 1.4 and 2.0 Å, respectively. These values of R are indicated by *vertical lines* denoted by EN and MP

Fig. 6. H_2 computed using using the MP (*squares*), EN (*circles*), and MAXR_c (*crosses*) partitioning methods at the equilibrium geometry for the FCI ($R = 0.735$ Å) up to $N = 10$. The energy axis corresponds to ($E_N - E_\infty$), where E_N is the Nth- order energy and E_∞ is the infinite-order result obtained from the FCI

The order-by-order results for H_2 at an internuclear distance of 0.735 Å, corresponding to the equilibrium geometry for the FCI, are given in Fig. 6. At this geometry, the EN and MAXR_c methods converge rapidly. The MP method performs poorly compared to the other two methods. At an internuclear distance of 1.8 Å, given by Fig. 7, EN yields little or no useful information: The second order is better than the first; the third, fourth and fifth orders offer no improvement; the sixth order marks the onset of divergent behavior. The other two methods perform satisfactorily at this geometry. At 2.4 Å, given by Fig. 8, EN diverges in low orders. MP exhibits oscillatory behavior and a divergent expansion with little useful information. MAXR_c converges, but slowly, as expected.

The potential-energy curve for HF computed through the tenth order ($N = 10$) for geometries between 0.6 and 2.0 Å is presented in Fig. 9. All methods agree with the FCI (the solid line) in the well region. EN exhibits a large deviation from the FCI beyond about 1.6 Å. A noticeable deviation from the FCI is found for the MP and MAXR_c methods in the vicinity of 2.0 Å. This
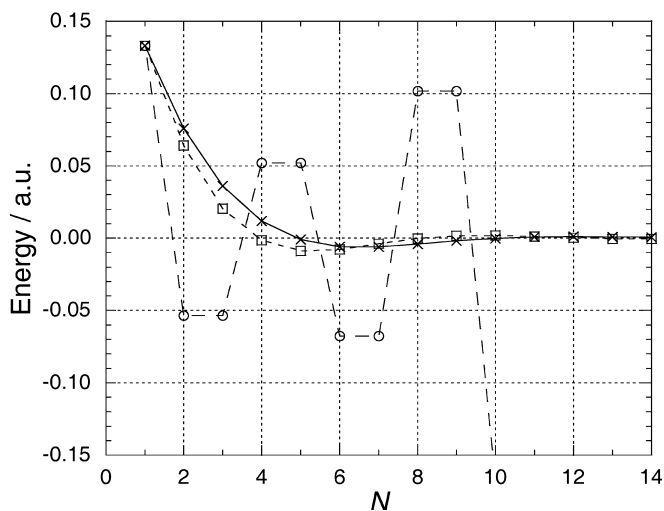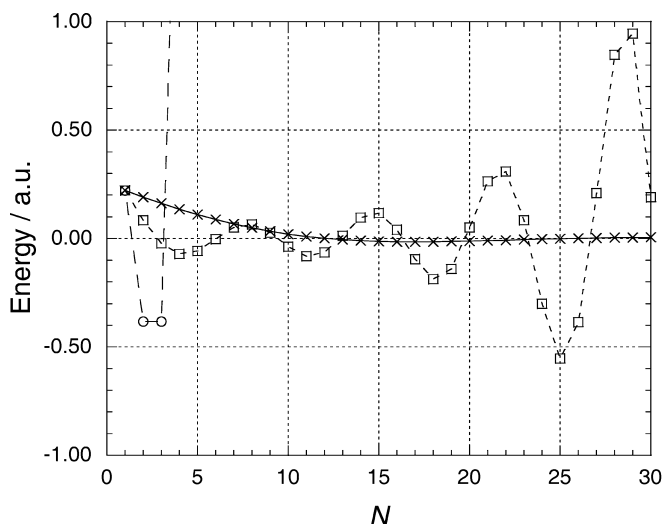
behavior is anticipated for large bond distances, where the reference state offers a poor description of the target state see Fig. 5. We have also performed higher-order calculations ($10 < N < 100$) and found that EN and MP partitioning methods yield divergent expansions for internuclear distances greater than about 1.6 and 1.9 Å, respectively. These values of R are indicated by vertical lines, denoted by EN and MP. At these geometries the weights ($|C_{ref}|^2$) of the reference determinant for the FCI wavefunction are 0.83 and 0.71, respectively. The weights over all geometries considered are given by the dashed line in Fig. 5. The points where MP ($\square$) and EN ($\bigcirc$) first diverge are indicated in the figure.
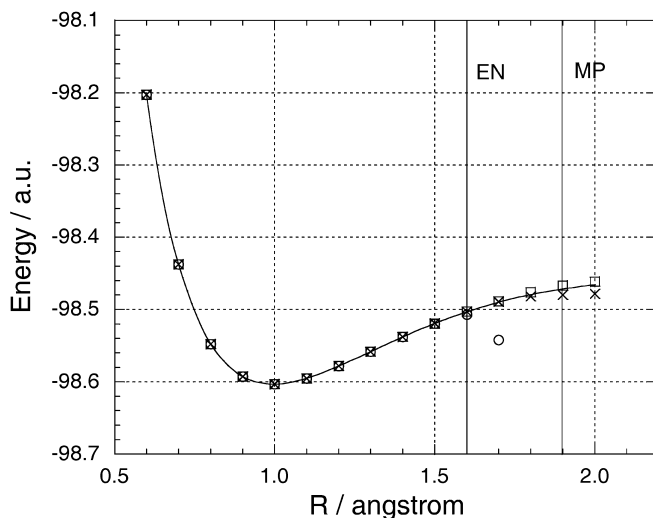

Fig. 9. The potential energy curve of HF computed using the three partitioning methods for $N = 10$. The *solid line* denotes the exact FCI curve. From higher-order calculation (up to $N = 100$) it can be shown that EN and MP partitioning methods yield divergent expansions for internuclear distances greater than about 1.6 and 1.9 Å, respectively. These values of R are indicated by *vertical lines* denoted by EN and MP
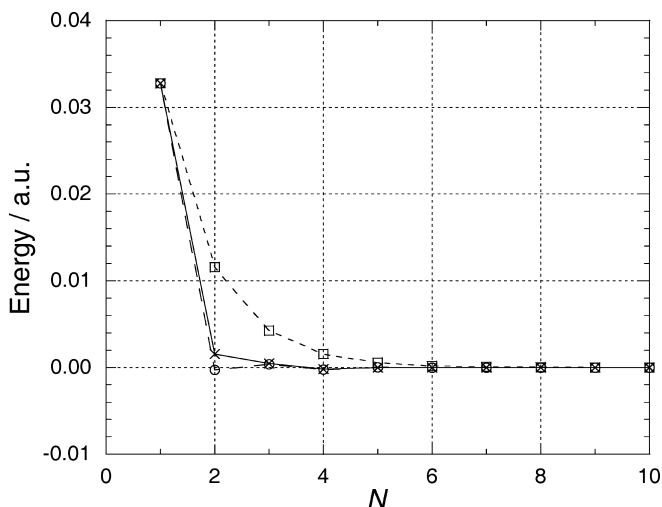

Fig. 7. Same as Fig. 6 but at $R = 1.8$ Å

Fig. 8. Same as Fig. 6 but at $R = 2.4$ Å

Fig. 10. HF computed using using the MP (*squares*), EN (*circles*), and MAXR_c (*crosses*) partitioning methods near the equilibrium geometry ($R = 1.0$ Å) upto $N = 10$. The energy axis corresponds to ($E_N - E_\infty$), where E_N is the Nth-order energy and E_∞ is the infinite-order result obtained from the FCI
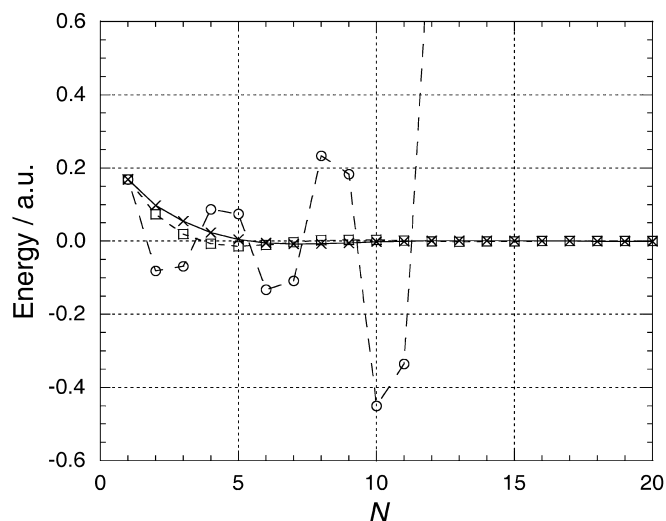
Fig. 11. Same as Fig. 10 but at $R = 1.8$ Å

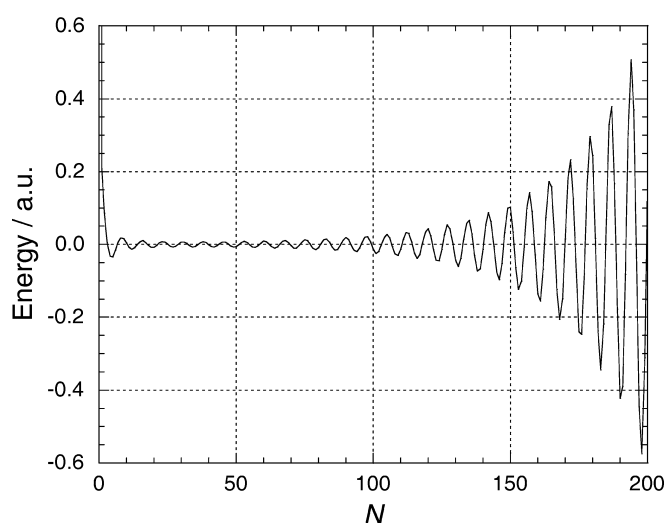**Fig. 12.** The divergent behavior of MP partitioning methods for HF at $R = 1.8$ Å

The low order results for HF at an internuclear distance of 1.0 Å, corresponding to the equilibrium geometry, are presented in Fig. 10. At this geometry MP performs poorly compared to the other two methods, which converge rapidly. At 1.8 Å, given by Fig. 11, EN rapidly diverges, while MP and MAXR_c both perform in a similar manner. However, MP eventually diverges in very higher orders, given by Fig. 12.

4 Conclusion

For the systems we have examined, MP and EN frequently perform poorly; these methods often diverge or, compared to the MAXR_c method, converge slowly. MAXR_c consistently performs well, except at very large bond distances where convergence can be very slow; but, this is anticipated. Such cases can be treated by multireference perturbation theory. MAXR_c is compatible with multireference perturbation theory, but requires some modifications when a Fock space formulation is employed.

Since we have used only small basis sets – a minimum basis set in all cases except for neon – and examined only a few small systems, caution should be exercised when generalizing these results to larger basis sets and for larger systems. However, even if it is later demonstrated that MAXR_c performs poorly in these more challenging cases, we believe that MAXR_c partitioning possesses features that are needed to obtain satisfactory convergence for any "new and improved" partitioning method. Consider, for example, a typical perturbation calculation involving a reference state and, say, n orthogonal-space states. For a "new and improved" partition method, a convergent series should arise from any two-state calculation involving – exclusively – the reference state and any selected orthogonal state, i.e., any one of the n orthogonal-space states is selected for a two-state calculation.

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