

On the inherent divergence in the Møller–Plesset series. The neon atom – a test case

Ove Christiansen ^a, Jeppe Olsen ^b, Poul Jørgensen ^a, Henrik Koch ^a,
Per-Åke Malmqvist ^b

^a Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

^b Chemistry Center, University of Lund, Box 124, S-22100 Lund, Sweden

Received 22 July 1996

Abstract

It has recently been shown that Møller–Plesset perturbation calculations may diverge for single configuration dominated systems in extended basis sets. We examine the origin of this divergence using the neon atom as a test example. The lowest energies for total symmetric states are calculated for values of the perturbation parameter strength $z \in [-1, 1]$. For $z \approx (-0.9) - (-0.8)$ avoided crossings between the Hartree–Fock configuration dominated state and states dominated by quintuple and higher excitations are observed. The origin of the divergence is therefore “back door” intruder states, that are highly excited relative to the Hartree–Fock state.

1. Background

It has been a general, but implicit, assumption in quantum chemistry that Møller–Plesset perturbation theory [1] converges well for single configuration dominated systems. This was supported by several high order perturbation calculations using full configuration interaction (FCI) programs [2–4], as well as calculations through sixth order using recent progress in explicit programmed Møller–Plesset perturbation theory [5]. In a recent paper [6] we found a surprising divergent behaviour in Møller–Plesset calculations for the single configuration dominated systems Ne, HF, H₂O and F⁻ using extended basis sets. In this Letter we investigate the origin of these divergences. Calculations on Ne will be used to exemplify and to illustrate the origin of the divergent behaviour.

In standard Møller–Plesset perturbation theory [1], the Hamilton operator is partitioned into a zeroth order part described by the Fock operator F and a perturbation operator. The perturbation is the fluctuation potential ϕ describing the difference between the true electron–electron repulsion and the Fock potential representation of the average electron–electron repulsion. Consider the Hamiltonian

$$H(z) = F + z\phi, \quad (1)$$

defined in terms of a complex strength parameter z . The physical Hamiltonian is represented by $H(1)$. The electronic Schrödinger equation for the Hamiltonian in Eq. (1) becomes, in a finite basis,

$$H(z)\psi(z) = \epsilon(z)\psi(z). \quad (2)$$

Møller–Plesset perturbation theory is defined as the Taylor expansion of the energy $\epsilon(z)$ around $z = 0$.

We denote the energy of this expansion $E(z)$ to distinguish it from the eigenvalue $\epsilon(z)$ in Eq. (2)

$$E(z) = \sum_{n=0}^{\infty} E^{(n)} z^n, \quad (3)$$

with $E^{(n)}$ being the n th order energy correction.

The convergence of the Møller–Plesset series in Eq. (3) depends on having a well separated energy spectrum for the zeroth order Hamiltonian ($z=0$) and for the physical problem ($z=1$). The expansion in Eq. (3) has a finite radius of convergence, R . A necessary condition for the convergence of $E(1)$ to $\epsilon(1)$ is that $R \geq 1$. The convergence radius depends on the behaviour of the eigenvalues $\epsilon(z)$ as functions of z in the complex plane. The eigenvalues $\epsilon(z)$ are branches of analytic functions. For physical reasons and because we express Eq. (2) in a finite basis we expect the eigenvalues $\epsilon(z)$ to be finite. The convergence radius is the distance from the expansion point (zero) to the nearest point of degeneracy of the functions $\epsilon(z)$ [7–9] (or nearest pole of $\epsilon(z)$). Degeneracies of $\epsilon(z)$ in the complex plane for $|z| \leq 1$ therefore lead to a divergent Møller–Plesset series. Since $(\epsilon(z^*))^* = \epsilon(z)$, degeneracies occur in complex pairs at z and z^* . It can be expected that the degeneracies will show up as an avoided crossing on the real axis [10–13] in the interval $-1 \leq z_{ac} \leq 1$.

It is well known that divergent perturbation series are often obtained in multiconfiguration dominated systems and excited states. The origin of the divergent behaviour in these problematic cases has been investigated by several authors [9–14]. Usually, the origin of the divergences is discussed in terms of intruder states. Both “front door” intruders ($z_{ac} > 0$) and “back door” intruders ($z_{ac} < 0$) have been found to be the cause of divergences.

2. Results

We have recently [6] reported the convergence behaviour of Møller–Plesset calculations on Ne using the cc-pVDZ [15], aug-cc-pVDZ [16] and cc-pVTZ [15] basis sets where in the cc-pVTZ basis the f function was left out (cc-pVTZ – (f)). The $1s$ orbital was frozen to the canonical Hartree–Fock

Table 1

MPn and FCI results for Ne in the aug-cc-pVDZ basis set. MPn energies are given as the deviation from FCI in millihartree (MPn – FCI, $E_{\text{FCI}} = -128.709476$ hartree). The $1s(\text{Ne})$ orbital is frozen. Results taken from Ref. [6]

MP1	213.126	MP23	0.244	MP45	9.148
MP2	6.252	MP24	-0.275	MP46	-11.007
MP3	4.705	MP25	0.313	MP47	13.251
MP4	-0.981	MP26	-0.359	MP48	-15.959
MP5	1.032	MP27	0.414	MP49	19.229
MP6	-0.550	MP28	-0.480	MP50	-23.176
MP7	0.409	MP29	0.559	MP51	27.942
MP8	-0.298	MP30	-0.655	MP52	-33.700
MP9	0.240	MP31	0.769	MP53	40.653
MP10	-0.200	MP32	-0.907	MP54	-49.052
MP11	0.175	MP33	1.072	MP55	59.199
MP12	-0.159	MP34	-1.270	MP56	-71.458
MP13	0.149	MP35	1.509	MP57	86.270
MP14	-0.144	MP36	-1.797	MP58	-104.167
MP15	0.142	MP37	2.143	MP59	125.795
MP16	-0.144	MP38	-2.559	MP60	-151.931
MP17	0.148	MP39	3.061	MP61	183.518
MP18	-0.156	MP40	-3.665	MP62	-221.694
MP19	0.166	MP41	4.393	MP63	267.836
MP20	-0.180	MP42	-5.272	MP64	-323.609
MP21	0.197	MP43	6.330	MP65	391.024
MP22	-0.218	MP44	-7.608		

orbital in all the calculations. We found that the Møller–Plesset series converges rapidly for the cc-pVDZ and cc-pVTZ (–f) basis, whereas the aug-cc-pVDZ series has a divergent and oscillating behaviour. In Table 1, we give the difference between the Møller–Plesset energy through a given order (MPn) and the full configuration interaction (FCI) energy for the aug-cc-pVDZ basis set. In Table 2 the orbital energies for the Hartree–Fock aug-cc-pVDZ calculation are given. From the orbital energies it is seen that the zeroth order spectrum is well separated. The energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO) is $1.14 E_h$. The weight of the

Table 2

Orbital energies in hartree, for Ne in the aug-cc-pVDZ basis set

s	p	d
-32.79495		
-1.94042	-0.85304	
0.28736	0.29301	1.75769
2.74197	1.96135	6.37247

Hartree–Fock determinant in the FCI wavefunction (W_{HF}) is 0.964. The W_{HF} and HOMO–LUMO gap are relevant parameters for the convergence of the Møller–Plesset series. For the abovementioned three basis sets we found in Ref. [6] that the W_{HF} is similar in the three calculations, clearly demonstrating the single configuration nature of the Ne ground state. The HOMO–LUMO gap differs in the three basis sets with the smallest gap in the aug-cc-pVDZ basis, but the $1.14 E_h$ is still a large gap. The numerical values of the MP_n contributions from consecutive orders start to increase beyond order fifteen. This divergent behaviour was surprising, in the sense that both the zeroth order energy spectrum and the physical spectrum is well separated. We found the same type of divergences and extreme dependency on the basis set in calculations in other systems HF, H_2O and F^- . In the following we will focus on the Ne aug-cc-pVDZ perturbation series.

As discussed previously, the Møller–Plesset series diverges if degeneracies appear in the energy spectrum of the Hamiltonian in Eq. (1) for real values of z , $|z| \leq 1$. We therefore carried out calcu-

lations of the total energies of the lowest states of the Hamiltonian in Eq. (1) for $-1 \leq z \leq 1$. The calculations were carried out with the LUCIA FCI program [17] using FCI techniques [18]. In Table 3 the values of the total energies of the ground and ^1S excited states are given for selected z values. Also given in Table 3 are the weights of various excitation levels with respect to the Hartree–Fock reference state. At $z = 1$, the ground state is dominated by the Hartree–Fock configuration. The first excited state is dominated by the $2p \rightarrow 3p$ excitation, while the second excited state is dominated by the $2s \rightarrow 3s$ excited configuration. The results in Table 3 confirm that the physical spectrum ($z = 1$) is well separated. The dominant configuration for the ground and first excited state for $z = 1$ is maintained in the whole interval for z larger than ≈ -0.6 .

In Fig. 1 the total energies of the three lowest states are plotted as a function of z . In Fig. 2, we display the energy difference between the total energy of the lowest excited states and the ground state total energy for the most interesting z interval. At $z \approx -0.7$, an avoided crossing occurs between the

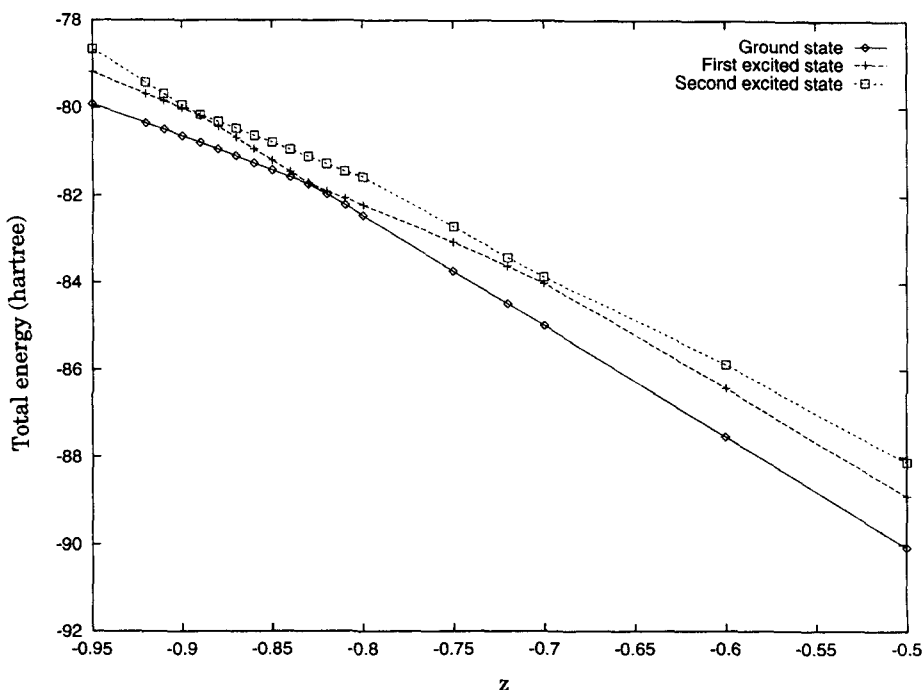


Fig. 1. Total energies in Hartree for the three lowest total symmetric singlet states as a function of the perturbation parameter z .

Table 3
Total energies (in hartree) for the three lowest 1S states for selected values of z

	State	1	2	3
$z = 1.0$	E	-128.70948	-127.86697	-127.01552
	0	0.9645	0.1755×10^{-2}	0.2461×10^{-3}
	1	0.9139×10^{-3}	0.9215	0.8191
	2	0.3378×10^{-1}	0.5817×10^{-1}	0.1518
	3	0.2998×10^{-3}	0.1627×10^{-1}	0.2568×10^{-1}
	4	0.4900×10^{-3}	0.2210×10^{-2}	0.2881×10^{-2}
	5	0.1343×10^{-4}	0.9923×10^{-4}	0.2327×10^{-3}
	6	0.2568×10^{-5}	0.1824×10^{-4}	0.2427×10^{-4}
	7	0.1150×10^{-6}	0.3654×10^{-6}	0.6675×10^{-6}
8	0.2062×10^{-8}	0.1847×10^{-7}	0.2694×10^{-7}	
$z = -0.2$	E	-97.72658	-96.55109	-95.49753
	0	0.9987	0.6264×10^{-5}	0.4203×10^{-4}
	1	0.2178×10^{-5}	0.9921	0.4633×10^{-2}
	2	0.1323×10^{-2}	0.6293×10^{-2}	0.9782
	3	0.8962×10^{-6}	0.1577×10^{-2}	0.1548×10^{-1}
	4	0.8305×10^{-6}	0.1915×10^{-4}	0.1548×10^{-1}
	5	0.1706×10^{-8}	0.1205×10^{-5}	0.3352×10^{-4}
	6	0.2231×10^{-9}	0.1451×10^{-7}	0.1043×10^{-5}
	7	0.5756×10^{-12}	0.2780×10^{-9}	0.1247×10^{-7}
8	0.1113×10^{-13}	0.1429×10^{-11}	0.1042×10^{-9}	
$z = -0.5$	E	-90.07578	-88.91532	-88.12980
	0	0.9913	0.3936×10^{-3}	0.2959×10^{-3}
	1	0.1146×10^{-3}	0.9163	0.6078×10^{-1}
	2	0.8508×10^{-2}	0.6013×10^{-1}	0.5674
	3	0.5213×10^{-4}	0.2040×10^{-1}	0.2402
	4	0.3843×10^{-4}	0.2369×10^{-2}	0.9805×10^{-1}
	5	0.7148×10^{-6}	0.3462×10^{-3}	0.2763×10^{-1}
	6	0.9168×10^{-7}	0.3248×10^{-4}	0.5184×10^{-2}
	7	0.2007×10^{-8}	0.2019×10^{-5}	0.4388×10^{-3}
8	0.5315×10^{-10}	0.6101×10^{-7}	0.1651×10^{-4}	
$z = -0.6$	E	-87.53412	-86.41148	-85.87297
	0	0.9870	0.1005×10^{-2}	0.1142×10^{-3}
	1	0.2713×10^{-3}	0.8345	0.9285×10^{-1}
	2	0.1247×10^{-1}	0.1050	0.1853
	3	0.1306×10^{-3}	0.4537×10^{-1}	0.2462
	4	0.8859×10^{-4}	0.1067×10^{-1}	0.2353
	5	0.2931×10^{-5}	0.2839×10^{-2}	0.1626
	6	0.4003×10^{-6}	0.5816×10^{-3}	0.6648×10^{-1}
	7	0.1633×10^{-7}	0.6914×10^{-4}	0.1055×10^{-1}
8	0.5770×10^{-9}	0.3729×10^{-5}	0.6267×10^{-3}	
$z = -0.7$	E	-84.99703	-84.00964	-83.85914
	0	0.9815	0.1462×10^{-2}	0.8284×10^{-3}
	1	0.5900×10^{-3}	0.2927	0.4665
	2	0.1739×10^{-1}	0.1201	0.4363×10^{-1}
	3	0.3092×10^{-3}	0.1253	0.1781×10^{-1}
	4	0.1944×10^{-3}	0.1381	0.6104×10^{-1}
	5	0.1252×10^{-4}	0.1562	0.1576
	6	0.2236×10^{-5}	0.1248	0.1838
	7	0.2193×10^{-6}	0.3616×10^{-1}	0.5943×10^{-1}
8	0.1609×10^{-7}	0.5225×10^{-2}	0.9396×10^{-2}	

Table 3 (continued)

	State	1	2	3
$z = -0.8$	E	-82.46492	-82.21762	-81.57100
	0	0.9735	0.7116×10^{-3}	0.4087×10^{-2}
	1	0.1250×10^{-2}	0.1152×10^{-2}	0.3596
	2	0.2365×10^{-1}	0.5648×10^{-2}	0.2013
	3	0.8012×10^{-3}	0.2676×10^{-1}	0.1803
	4	0.5245×10^{-3}	0.9663×10^{-1}	0.1014
	5	0.1503×10^{-3}	0.2425	0.2996×10^{-1}
	6	0.9927×10^{-4}	0.3668	0.4675×10^{-1}
	7	0.4004×10^{-4}	0.2021	0.5075×10^{-1}
8	0.9276×10^{-5}	0.5769×10^{-1}	0.2585×10^{-1}	
$z = -0.9$	E	-80.65279	-80.00597	-79.93783
	0	0.9831×10^{-5}	0.6323×10^{-2}	0.9557
	1	0.6964×10^{-4}	0.8422×10^{-3}	0.2347×10^{-2}
	2	0.6728×10^{-3}	0.4413×10^{-2}	0.3081×10^{-1}
	3	0.5217×10^{-2}	0.1882×10^{-1}	0.1330×10^{-2}
	4	0.3012×10^{-1}	0.7238×10^{-1}	0.9098×10^{-3}
	5	0.1197	0.1918	0.1708×10^{-2}
	6	0.2900	0.2765	0.3776×10^{-2}
	7	0.3497	0.1498	0.1439×10^{-2}
8	0.2045	0.2792	0.1945×10^{-2}	

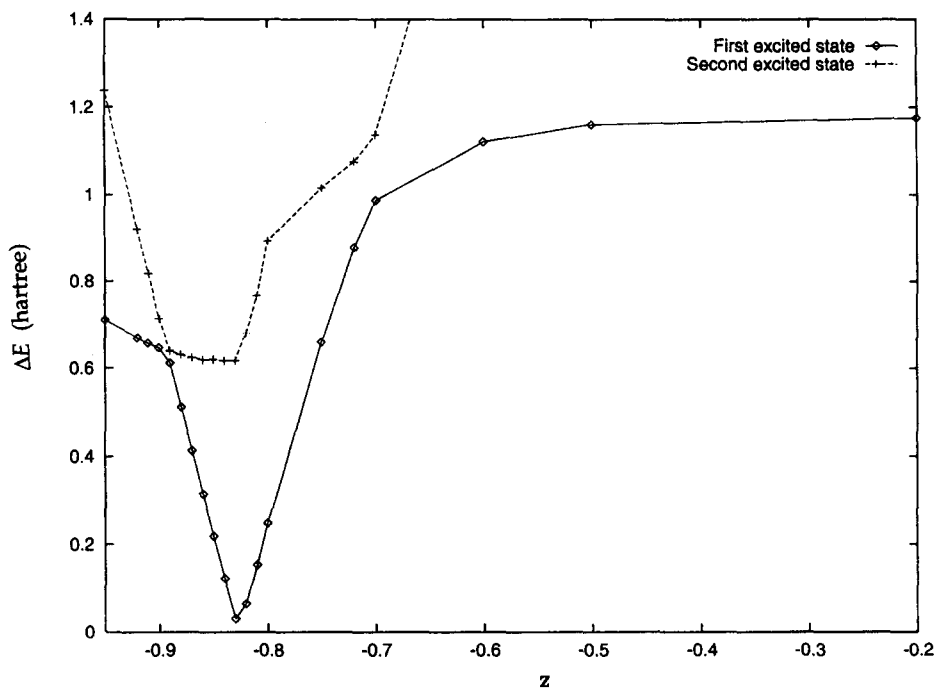


Fig. 2. The energy difference in hartree between the two lowest excited states and the ground state as a function of the perturbation parameter z .

first excited state and a state that is dominated by quintuple and higher excitations. An avoided crossing between this highly excited state and the Hartree–Fock configuration dominated state occurs at $z \approx -0.82$. For z larger than ≈ -0.82 , the lowest state is thus dominated by the Hartree–Fock configuration, whereas for $z < -0.82$, the lowest state is dominated by quintuple and higher excited configurations. The Hartree–Fock dominated state has another avoided crossing with the second excited state at $z \approx -0.89$. For $z = -0.9$, the reference state is thus the third state of 1S symmetry. Thus we clearly see that several intruder states enter for $|z| < 1$. The radius of convergence for the series is thus less than one, (0.8–0.9) giving a divergent Møller–Plesset series.

An important finding in these calculations is that the intruder states are highly excited relative to the Hartree–Fock reference. Typically, the intruder states are physical states that are energetically nearby for $z = 1$ [10–13]. A well separated energy spectrum for the physically relevant spectrum $z = 1$ and the zeroth order spectrum $z = 0$ does not guarantee convergence, since states of no physical interest may act as backdoor intruders. It is interesting to note that the Hartree–Fock dominated state undergoes more than one crossing with states that are highly excited. From Fig. 1 we observe that on a large scale the HF configuration dominated states follow almost a straight line as a function of z . The intruder states have a smaller slope for $z < -0.5$, and therefore undergo crossings with the reference configuration. The Hartree–Fock state is thus destabilized faster as z goes to -1 from the right, than are the highly excited intruder states.

The fluctuation potential describes the difference between the true electron–electron repulsion and the effective Fock potential. As such, the fluctuation potential contains both attractive and repulsive parts as a function of the interelectronic distance. For $z = 1$ the overall effect for the Hartree–Fock dominated state is stabilization. Correspondingly, we observe a destabilization for negative z . Highly diffuse and delocalized states may have a significantly different dependency on z than the localized Hartree–Fock state as different electronic structures give different distributions of interelectronic distances. Changing the sign of the fluctuation potential favours

different interelectronic distances. States that are very different from the Hartree–Fock dominated state in the electronic structure, may therefore be destabilized less than the Hartree–Fock state, and for some complex value of z these states may obtain a lower energy than the Hartree–Fock dominated state. This is in fact what is seen in Fig. 2. The exact position of the point of degeneracy will depend on the relative destabilization of the Hartree–Fock state and the other states. This relative destabilization of the Hartree–Fock state will in turn depend on the basis set and the nature of the electron distribution.

Including diffuse functions expands the region in which the electrons can move, and thus makes it possible to describe states which are highly diffuse and delocalized, i.e. states where more electrons are far away from each other. This may explain why in the cc-pVDZ basis set a convergent Møller–Plesset series is found, while in the aug-cc-pVDZ basis set, highly excited states become intruder states and causes divergences in the Møller–Plesset series. Furthermore, the more close-lying the electrons in the Hartree–Fock reference, the larger the relative energy advantage that may be obtained by redistributing the electrons in space. Divergent Møller–Plesset series were obtained for H_2O , HF, Ne and F^- in basis sets including diffuse functions. Convergent Møller–Plesset series were obtained in the less electron-rich but more multiconfiguration dominated molecules BH and CH_2 . We may thus expect that the divergent behaviour will become even more pronounced in more extensive basis sets and for systems with more electrons.

A number of schemes for transforming a slowly convergent – or divergent – series into a better convergent series have been devised. The Feenberg scaling method [19] has recently received special attention, partly due to its connection with the so-called λ -transformed perturbation theory [8–12,20]. Following Schmidt, Warken and Handy [20] we note that the use of Feenberg scaling in connection with MP theory, corresponds to the following repartitioning of the Hamiltonian

$$H(z, \lambda) = \frac{1}{1-\lambda}F + z \left(\varphi - \frac{\lambda}{1-\lambda}F \right). \quad (4)$$

The λ parameter is a parameter at the user's disposal, and should be chosen to make the conver-

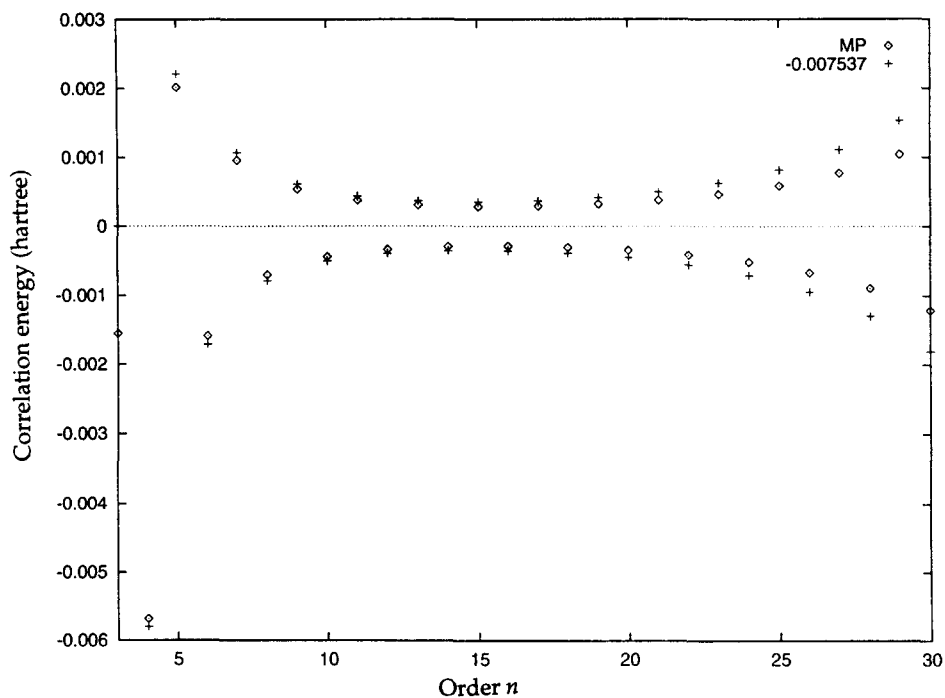


Fig. 3. Correlation contributions at different orders of the original Møller-Plesset series and the Feenberg transformed series where $\lambda = -0.007537$.

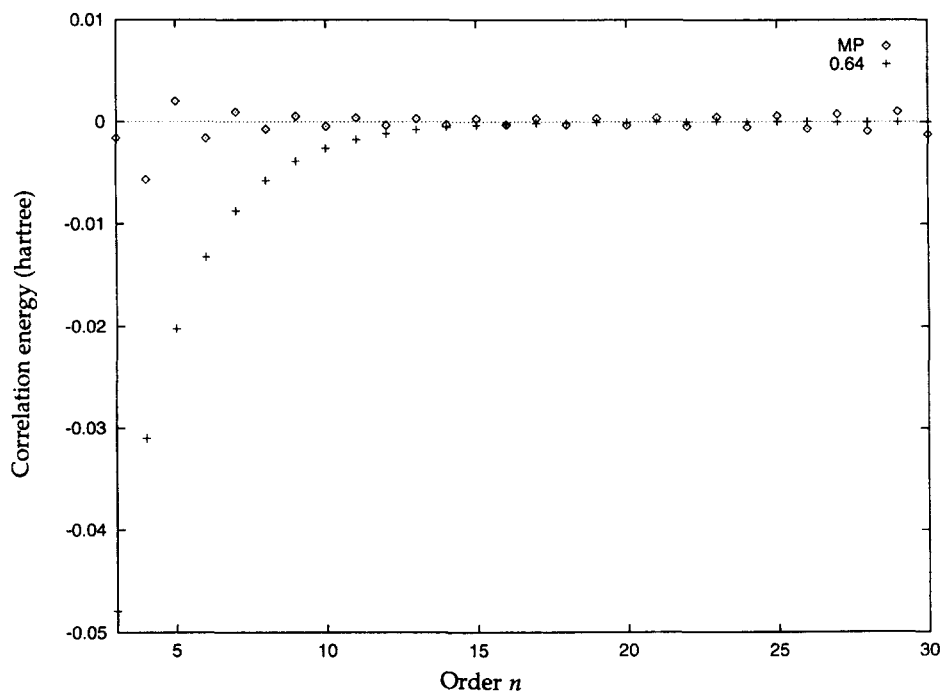


Fig. 4. Correlation contributions at different orders of the original Møller-Plesset series and the Feenberg transformed series where $\lambda = 0.64$.

gence optimal. Since the Hamiltonian is independent of λ for $z = 1$, a convergent sequence will converge to the same limit. However, since the Hamiltonian depends on λ for z different from 1, the convergence behaviour is a function of λ . The energy contributions ($\tilde{E}_n(\lambda)$) of the repartitioned Hamiltonian as in Eq. (4) can be related to the energy contributions of the original MP series as [20]

$$\tilde{E}_n(\lambda) = \sum_{k=1}^n \binom{n-2}{k-1} \lambda^{n-k-1} (1-\lambda)^k E^{(k+1)},$$

$$n \geq 2, \quad (5)$$

The parameter λ is usually chosen so that the third order energy correction vanishes; i.e.

$$\lambda = 1 - \frac{E^{(2)}}{E^{(2)} - E^{(3)}}. \quad (6)$$

Provided that the energy corrections form a geometric sequence i.e. the ratio between energy contributions $E^{(n+1)}$ and $E^{(n)}$ is a constant independent of n , the exact energy is obtained to second order of the transformed series, and the third and higher order corrections vanish.

In Fig. 3 we have plotted the convergence of the Feenberg series for the choice of λ in Eq. (6). The original MP series corresponding to $\lambda = 0$ is provided for reference. The choice $\lambda = -0.007537$ obtained from Eq. (3) does not modify the MP sequence significantly, the series is still oscillating and diverges. Using a larger negative shift, -0.1 , leads to a faster divergent expansion. The use of positive values of λ stabilizes the series. For example, using $\lambda = 0.16$ one obtains an expansion free of oscillations in the first eight orders, and the total energies from order eight to twenty are close to the FCI energies. Divergence is, however, observed at higher orders. With a large positive shift, $\lambda = 0.64$, one obtains a nearly monotonic sequence, without any signs of divergence through the first 65 orders. In Fig. 4 we have plotted this series together with the original MP series. It is seen that the rate of convergence in the Feenberg series is now slow; the energy corrections decrease typically by less than a factor of 1.5 in each of the first twenty orders, and to obtain an energy error of less than $10^{-3} E_h$, it is necessary to proceed through order 15.

The Feenberg scaling method is thus not sufficient to change the current MP sequence to a fast convergent series. It is not surprising that the standard value of λ does not lead to convergence, since the divergent behaviour first starts at higher order. It is evident that our perturbation series is not well described by a geometric progression. Increasing λ to large positive values, enlarges the zeroth energy separation and seemingly a convergent series is obtained. However, the rate of convergence is now slow. This exhibits clearly the conflict between obtaining a good wavefunction at low order (first and second order), and obtaining a series that gives good overall convergence.

3. Conclusion

Møller–Plesset perturbation theory is one of the most commonly used methods for including dynamic correlation in electronic structure calculations and it is therefore important to understand its convergence behaviour. Second order Møller–Plesset calculations give remarkably good results and it is the simplest and most widespread method for treating dynamical correlation. During the last decade it has been still more common to carry out Møller–Plesset perturbation calculations through fourth order and recently explicit calculations of the fifth and sixth order terms have been reported [5]. This development towards extending Møller–Plesset calculations through still higher order emphasizes the importance of understanding more fully the convergence behaviour of the perturbation series.

In a recent paper, we have shown that Møller–Plesset perturbation calculations may diverge in extended basis sets, even for single configuration dominated molecules. Divergent behaviour was found for H_2O , HF, Ne and F^- using basis sets containing diffuse functions. In this Letter, we have examined the origin of this divergence by carrying out additional calculations on Ne.

For convergence of a Møller–Plesset perturbation series, it is a necessary, but not sufficient, condition that the energy spectrum is well separated for the physical spectrum where the perturbation is turned on ($z = 1$) and also for the zeroth order spectrum where the perturbation is absent ($z = 0$). In both

cases, this is satisfied for the Ne calculation where the Møller–Plesset series showed a divergent behaviour. A Møller–Plesset series will diverge if degeneracies in the energy spectrum for $|z| \leq 1$ are present. For $z \approx -0.82$, we have found an avoided crossing between the Hartree–Fock configuration dominated state and a state dominated by quintuple and higher excitations. The Hartree–Fock dominated state that in Møller–Plesset perturbation theory is assumed to be the lowest state is thus for z smaller than ≈ -0.82 an excited state. We thus have degeneracies for $|z| \leq 1$, and a divergent Møller–Plesset series is consequently obtained.

The lowest order Møller–Plesset energy contributions may still contain a large fraction of the correlation energy and useful physical information may be obtained from the lowest order contributions. However, it is extremely difficult to decide a priori to what extent the perturbation calculation is meaningful. For example, in a calculation on F^- which also had a well separated energy spectrum for $z = 0$ and $z = 1$, the divergent behaviour started at third order while for Ne, it started at a much higher order [6]. The divergent behaviour has so far only been found in extended basis set calculations. However, extended basis sets are necessary to describe many physical situations, for example, in calculations on anions and excited states and also for the determination of such fundamental molecular properties as the dipole moment and polarizability. Thus the use of extended basis sets cannot be avoided. Since the intruder states causing the divergence are non-physical, it is extremely difficult to predict a priori the convergence behaviour of a Møller–Plesset perturbation series without explicitly studying the spectrum of $H(z)$ for $|z| \leq 1$. The strong dependence on the basis set reported previously certainly does not improve this aspect. We therefore cannot advise the use of higher order perturbation calculations as a vehicle for obtaining increasing accuracy of quantum chemical calculations.

The highly excited nature of the intruder states makes the approach of increasing the size of the reference space [9–14] of little practical value. Investigations of the energy spectrum for $-1 \leq z \leq 1$ based on restricted excitation spaces e.g. single and double excitations is not reliable either. It was demonstrated that resummation techniques seem-

ingly eliminate the divergences to arbitrary order at the price of a slowly convergent expansion in low order. However, in our opinion high order perturbation theory will not be valuable as a practical approach if it only has meaning in connection with resummation techniques. The advantage of the Møller–Plesset partitioning is that it gives a good zeroth and first order wavefunction in single configuration dominated cases and the simplest MP2 method may still be a valuable tool for computational chemistry. However, it is probably advantageous to turn to other approaches for obtaining hierarchies of approximations that in a systematic fashion give results of increasing accuracy.

Acknowledgement

This work has been supported by the Danish Natural Science Research Council (Grant No. 11-0924) and the Swedish Natural Research Council (NFR).

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