On the convergence of the Møller–Plesset perturbation series

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Møller–Plesset perturbation energies, up to as much as 48th order, have been calculated for H_2O (RHF and UHF framework) and NH_2 (UHF framework) at C_{2v} geometries (r_e, $1.5r_e$ and $2r_e$). At r_e, the RHF and UHF series rapidly converge, but at $2r_e$, the RHF series converges erratically with an energy at 43rd order within 10^{-7} hartree of the exact value whereas the UHF series converges smoothly, but very slowly, and for H_2O has an error in excess of 10^{-5} hartree at 48th order. The significance of these results is discussed.

Key words: Perturbation series convergence

1. Introduction

Elsewhere [1], we have briefly reported our investigations into the convergence of the Møller–Plesset [2] perturbation series for the energy of a molecule. In this paper we shall report our most detailed calculations. In the most common applications of this perturbation theory, the zeroth order hamiltonian H_0 is the sum of one electron Fock operators, derived from Restricted Hartree–Fock (RHF) theory for closed shell systems and Unrestricted Hartree–Fock (UHF) theory for open shell systems. The results we have obtained are given in detail so that other workers may have the opportunity of observing the convergence of the series for these examples.

The reason for these investigations is the wide use of the Møller–Plesset (MP) series for the inclusion of electron correlation effects into energy calculations. Pople and his co-workers [3, 4] especially have made much use of this approach because of the significant percentage (typically 75%) of the correlation energy which can be achieved using third order perturbation (MP3) theory. The calculation of MP2 and MP3 energies is straightforward and fast, and has been made

generally available to chemists through the distribution of GAUSSIAN 80 [3]. For higher accuracy, it has been claimed that the calculation of MP4 energies (including single, double, triple, and quadruple substitutions) makes a substantial improvement on the calculations of structural properties, and this has been supported by many investigations. MP4 energies are also fairly easy to calculate for small and medium sized basis set at least, and this has been made available through GAUSSIAN 82 [4]. However it seems clear that the routine calculation of higher order perturbation energies for large basis sets will be impossible. Although we have concentrated on the Møller–Plesset series in this paper, the results will be of interest to those who are concerned with Many Body perturbation theory in its more general forms [5].

Our purpose here is not to enter into the discussion of the predictive properties of MP3 or MP4 except to observe that these series have the important property of size-consistency, but instead to address the problem of the convergence of the MP series in general. The relevant questions would appear to be:

(a) Is the MP series convergent?

(b) If the MP series is convergent, is it rapidly convergent?

(c) Are there formulae, such as Pade approximants, based on the first four or five terms in the series, which accurately predict the series limit, if it exists?

It appears that it is not possible to answer these questions in a general theoretical manner, and so we have attempted to do the next best, which is to take some special examples, and calculate the higher order terms in the series. That we are in a unique position to do this follows because we have recently developed a vectorised full-CI algorithm [6], and, as shown in the next section, this means it is a straightforward matter to calculate the perturbation series, term by term, for those systems for which it is possible to perform full-CI calculations.

The size of the calculation which we can consider is therefore restricted by the number of expansion functions (in our case single determinants) in the full-CI. However it is desirable to have more than four active electrons (because all possible excitations are met in MP4 for four electron systems), and also an adequately large basis set. It is also desirable to examine cases where the leading determinant has various degrees of dominance. For all these reasons, the examples selected were H_2O, with a 6-21G basis set, and NH_2, with a 6-31G basis set, in C_{2v} symmetry. On each, calculations were performed at r_e (an equilibrium bond length), $1.5r_e$ and $2r_e$. In common with the usual procedure in MP calculations, the core orbital was frozen. Energies up to as much as 48th order are calculated.

In section 3 the results of the calculations are given in detail, and in section 4 they are discussed.

2. Method

The elementary Rayleigh–Schrodinger perturbation theory to determine the terms in the MP series has been given in our earlier publication [1], and will not be

reproduced here. The result was that if intermediate normalisation is used, $\langle \psi_k | \psi_0 \rangle = 0$, $k > 0$, then the kth order energies E_k and wave functions ψ_k are given by

$$E_k = \langle \psi_0 | \sigma_k \rangle \tag{1}$$

$$\psi_k = (H_0 - E_0)^{-1} \left[\sum_{r=1}^{k} E_r \psi_{k-r} + H_0 \psi_{k-1} - \sigma_k \right] \tag{2}$$

with

$$\sigma_k = H \psi_{k-1} \tag{3}$$

(Of course the standard Wigner formulae may be used to obtain E_{2k}, E_{2k+1} from ψ_k, but we did not do so here.) The vectors σ_k are calculated by the full-CI program. If $H_0 = F$, the sum of one electron Fock operators, then H_0 is diagonal in the basis of single determinants, and so it is a straightforward matter to calculate ψ_k through Eq. (2).

There are two distinct cases to consider (i) singlets for which RHF orbitals are usually used and (ii) open-shell systems, for which UHF orbitals (i.e. different orbitals for different spins) are used. Thus far the full-CI algorithm has always been used in the framework of RHF orbitals, and a slight adjustment is necessary to consider the UHF case. This is demonstrated by considering the evaluation of the two electron integral contribution to the vector σ. In the algorithm it is evaluated through Siegbahn's [7] formula for the Ith component of the vector, the difficult part of which is:

$$\sigma_I = \tfrac{1}{2} \sum_K \sum_{kl} \gamma_{kl}^{KI} \sum_{ij} (ij|kl) \sum_J \gamma_{ij}^{JK} c_J, \tag{4}$$

with

$$\gamma_{ij}^{IJ} = \langle I | E_{ij} | J \rangle, \tag{5}$$

where $|I\rangle$ refer to determinants and E_{ij} is a unitary group one particle generator [8]. This generator can be written

$$E_{ij} = E_{ij}^{\alpha} + E_{ij}^{\beta}, \tag{6}$$

where E_{ij}^{α} excites one electron from α spin orbital j and α spin orbital i. Attaching spin labels to the orbitals, the formula for σ_I becomes

$$\sigma_I = \tfrac{1}{2} \sum_K \sum_{\nu=\alpha,\beta} \sum_{kl} \gamma_{k_\nu l_\nu}^{KL} \sum_{\mu=2\beta} \sum_{ij} (i_\mu j_\mu | k_\nu l_\nu) \sum_J \gamma_{i_\mu j_\mu}^{JK} c_J. \tag{7}$$

For the RHF formalism, the spin orbitals can be omitted from the integrals, and these molecular orbital integrals can be obtained from an ordinary 4-index transformation. In the UHF formalism, the spin labels have to be retained. Therefore a special 4-index transformation program was written to generate the sets of two electron integrals labelled by spins as $(\alpha\alpha|\alpha\alpha)$, $(\alpha\alpha|\beta\beta)$, $(\beta\beta|\alpha\alpha)$ and $(\beta\beta|\beta\beta)$. This was the only significant change to the full-CI algorithm which was necessary.

Table 1. Møller–Plesset perturbation energies for H_2O (C_{2v}, $r_e = 0.967$ Å, $\theta = 107.6°$, 6-21G basis, frozen core), using RHF orbitals

	r_e	$1.5r_e$	$2r_3$
$E_0 + E_1$	−75.888430	−75.707206	−75.491406
E_2	−0.120865	−0.166896	−0.241643
E_3	−0.003303	−0.002015	+0.006123
E_4	−0.004849	−0.016925	−0.046465
E_5	−0.000488	−0.001352	−0.004219
E_6	−0.000435	−0.003416	−0.012369
E_7	−0.000076	−0.000338	−0.001032
E_8	−0.000048	−0.000827	−0.004065
E_9	−0.000012	−0.000032	+0.002319
E_{10}	−0.000006	−0.000189	−0.001417
E_{11}	−0.000002	+0.000010	+0.002191
E_{12}	-10^{-6}	−0.000032	−0.000277
E_{13}	-10^{-7}	+0.000007	+0.000959
E_{14}	-10^{-7}	-10^{-6}	+0.000023
E_{15}	-10^{-7}	$+10^{-6}$	+0.000146
E_{16}	-10^{-8}	$+10^{-6}$	+0.000025
E_{17}	-10^{-8}	$+10^{-6}$	−0.000140
E_{18}	-10^{-9}	$+10^{-6}$	+0.000043
E_{19}	-10^{-9}	$+10^{-7}$	−0.000159
E_{20}	-10^{-9}	$+10^{-6}$	+0.000087
E_{21}	-10^{-10}	$+10^{-7}$	−0.000095
E_{22}	-10^{-10}	$+10^{-7}$	+0.000095
E_{23}	-10^{-10}	$+10^{-8}$	−0.000037
E_{24}	-10^{-11}	$+10^{-8}$	+0.000064
E_{25}			−0.000010
E_{26}			+0.000022
E_{27}			−0.000003
E_{28}			−0.000006
E_{29}			−0.000001
E_{30}			−0.000016
E_{31}			+0.000002
E_{32}			−0.000014
E_{33}			+0.000005
E_{34}			−0.000007
E_{35}			+0.000005
E_{36}			−0.000002
E_{37}			+0.000004
E_{38}			$+10^{-7}$
E_{39}			$+10^{-6}$
E_{40}			$+10^{-6}$
E_{41}			-10^{-7}
E_{42}			$+10^{-6}$
E_{43}			-10^{-6}
$\sum_2^4 E_i$	−0.129017	−0.185835	−0.281986
$\sum_2^{43} E_i$	−0.130085	−0.191996	−0.299864
"Exact" correlation energy	−0.130085	−0.191996	−0.299864

3. Calculations and results

As stated in the introduction, calculations have been performed on H_2O ($^1A_1$) and NH_2 ($^2B_1$) in C_{2v} geometry at bond lengths r_e, $1.5r_e$, and $2r_e$. For H_2O, $r_e = 0.967$ Å and $\theta = 107.6°$ (6-21G basis set was used); for NH_2 $r_e = 1.013$ Å and $\theta = 103.2°$ (6-31G basis set was used) [8]. In the calculations the core orbital was frozen. This meant the numbers of expansion determinants $|I\rangle$ and intermediate determinants $|K\rangle$ (see Eq. (4)) for H_2O were 61 441 and 245 025, and for NH_2 27 126 and 108 900. On the CRAY-1S, the calculation of 48 energies used 13 minutes cpu time, for H_2O at one geometry.

In Tables 1, 2 and 3 the results are given for H_2O and NH_2. For H_2O results at r_e, $1.5r_e$ and $2r_e$ are given for RHF orbitals in Table 1. It is also possible to consider UHF calculations for H_2O, even though this is not usually considered in MP calculations. At r_e, UHF = RHF, but at $1.5r_e$ and $2r_e$ they are different, and results are given for these geometries in Table 2. For NH_2 results at r_e, $1.5r_e$ and $2r_e$ are given for UHF orbitals.

Table 2. Møller-Plesset perturbation energies for H_2O (C_{2v}, $r_e = 0.967$ Å, $\theta = 107.6°$, 6-21G basis, frozen core), using UHF orbitals

	$1.5r_e$	$2r_e$		$1.5r_e$	$2r_e$
$E_0 + E_1$	−75.735012	−75.699298	E_{29}	−0.000167	−0.000341
E_2	−0.094376	−0.055371	E_{30}	−0.000126	−0.000334
E_3	−0.007435	−0.005550	E_{31}	−0.000090	−0.000327
E_4	−0.011388	−0.002203	E_{32}	−0.000059	−0.000320
E_5	−0.005684	−0.000948	E_{33}	−0.000033	−0.000313
E_6	−0.006457	−0.000847	E_{34}	−0.000011	−0.000307
E_7	−0.004832	−0.000659	E_{35}	+0.000007	−0.000301
E_8	−0.004687	−0.000636	E_{36}	+0.000022	−0.000295
E_9	−0.003920	−0.000578	E_{37}	−0.000035	−0.000289
E_{10}	−0.003577	−0.000562	E_{38}	+0.000044	−0.000283
E_{11}	−0.003099	−0.000534	E_{39}	+0.000052	−0.000278
E_{12}	−0.002761	−0.000519	E_{40}	+0.000057	−0.000272
E_{13}	−0.002415	−0.000501	E_{41}	+0.000061	−0.000267
E_{14}	−0.002128	−0.000488	E_{42}	+0.000063	−0.000262
E_{15}	−0.001861	−0.000474	E_{43}	+0.000064	−0.000257
E_{16}	−0.001629	−0.000461	E_{44}	+0.000063	−0.000252
E_{17}	−0.001419	−0.000449	E_{45}	+0.000062	−0.000248
E_{18}	−0.001234	−0.000438	E_{46}	+0.000060	−0.000243
E_{19}	−0.001068	−0.000428	E_{47}	+0.000057	−0.000238
E_{20}	−0.000922	−0.000417	E_{48}	+0.000054	−0.000234
E_{21}	−0.000791	−0.000408	$\sum_{2}^{4} E_i$	−0.113199	−0.063124
E_{22}	−0.000675	−0.000398			
E_{23}	−0.000573	−0.000389	$\sum_{2}^{48} E_i$	−0.164416	−0.080743
E_{24}	−0.000482	−0.000380			
E_{25}	−0.000402	−0.000372	"Exact"		
E_{26}	−0.000331	−0.000364	correlation		
E_{27}	−0.000269	−0.000356	energy	−0.164168	−0.091882
E_{28}	−0.000215	−0.000348			

It is possible to obtain the "exact" eigenvalue of H within these basis sets and with the frozen core orbitals, either using the full-CI program (in the RHF case) or variation perturbation theory. These exact eigenvalues are given in the tables to the number of significant figures to which they have converged.

It is constructive to look at the convergence of the series graphically, and therefore Fig. 1–7 show this convergence for higher terms in the series.

The question may arise as to whether the results are numerically stable. The answer to this is indicated from the results for H_2O (RHF) at $2r_e$, which clearly show ultimate convergence to the full-CI value only at a very high order, despite earlier erratic behaviour. In addition, in order to avoid problems arising from the strong linear dependencies amongst the successive ψ_k, our program employed a set of carefully orthogonalised functions

$$v_k = \alpha\left(\psi_k - \sum_{l=0}^{k-1} \langle v_l | \psi_k \rangle v_l\right); \qquad \langle v_k | v_k \rangle = 1, \tag{8}$$

with the actual ψ_k then represented as a linear combination

$$\psi_k = \sum_{l=1}^{k} c_{lk} v_k. \tag{9}$$

Table 3. Møller-Plesset perturbation energies for NH_2 (C_{2v}, $r_e = 1.013$ Å, $\theta = 103.2°$, 6-31G basis, frozen core), using UHF orbitals

	r_e	$1.5r_e$	$2r_e$
$E_0 + E_1$	−55.532248	−55.405143	−55.381931
E_2	−0.085512	−0.062116	−0.031539
E_3	−0.009815	−0.011394	−0.006208
E_4	−0.003613	−0.008695	−0.002508
E_5	−0.001192	−0.005776	−0.001234
E_6	−0.000463	−0.004887	−0.000846
E_7	−0.000200	−0.004067	−0.000662
E_8	−0.000100	−0.003505	−0.000568
E_9	−0.000053	−0.003016	−0.000507
E_{10}	−0.000030	−0.002608	−0.000464
E_{11}	−0.000018	−0.002254	−0.000432
E_{12}	−0.000011	−0.001949	−0.000406
E_{13}	−0.000007	−0.001684	−0.000384
E_{14}	−0.000005	−0.001454	−0.000364
E_{15}	−0.000003	−0.001254	−0.000347
E_{16}	−0.000002	−0.001080	−0.000332
E_{17}	−0.000001	−0.000929	−0.000318
E_{18}	-10^{-6}	−0.000798	−0.000305
E_{19}	-10^{-6}	−0.000684	−0.000293
E_{20}	-10^{-7}	−0.000584	−0.000282
E_{21}	-10^{-7}	−0.000499	−0.000272
E_{22}	-10^{-7}	−0.000424	−0.000262
E_{23}	-10^{-7}	−0.000360	−0.000253
E_{24}	-10^{-7}	−0.000304	−0.000245

Table 3. (*contd.*)

	r_e	$1.5r_e$	$2r_e$
E_{25}	-10^{-7}	-0.000256	-0.000237
E_{26}	-10^{-8}	-0.000214	-0.000229
E_{27}	-10^{-8}	-0.000178	-0.000222
E_{28}	-10^{-8}	-0.000148	-0.000216
E_{29}	-10^{-8}	-0.000122	-0.000209
E_{30}	-10^{-8}	-0.000099	-0.000203
E_{31}	-10^{-8}	-0.000080	-0.000198
E_{32}	-10^{-9}	-0.000064	-0.000192
E_{33}	-10^{-9}	-0.000050	-0.000187
E_{34}	-10^{-9}	-0.000039	-0.000182
E_{35}	-10^{-9}	-0.000029	-0.000178
E_{36}	-10^{-9}	-0.000021	-0.000173
E_{37}	-10^{-9}	-0.000014	-0.000169
E_{38}	-10^{-9}	-0.000009	-0.000165
E_{39}	-10^{-10}	-0.000004	-0.000161
E_{40}	-10^{-10}	-0.000001	-0.000157
E_{41}	-10^{-10}	$+0.000002$	-0.000153
E_{42}	-10^{-10}	$+0.000004$	-0.000150
E_{43}	-10^{-10}	$+0.000005$	-0.000147
E_{44}		$+0.000007$	-0.000143
E_{45}		$+0.000007$	-0.000140
$\sum_{2}^{4} E_i$	-0.098939	-0.082204	-0.040255
$\sum_{2}^{45} E_i$	-0.101028	-0.121622	-0.052847
"Exact" correlation energy	-0.101028	-0.121515	-0.059

As a further check, the arithmetic involving the c_{lk} arising from equation (2) was performed in double precision (128 bits); the results were identical to those obtained in single precision. Our conclusion is that the quoted results are numerically stable.

4. Discussion

In the Tables there are eight sets of results, and first we will discuss these individually.

(i) H_2O, r_e, RHF

This MP series is rapidly convergent, and the numbers of terms after E_0 needed so that the energy within 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} hartree of the exact value are 7, 8, 10, 13. However the very rapid early convergence is not maintained: $E_2/E_4 = 24.9$, $E_4/E_6 = 11.15$, $E_6/E_8 = 9.1$, $E_8/E_{10} = 8.0$. Figure 1 shows a smooth convergence to the exact value.
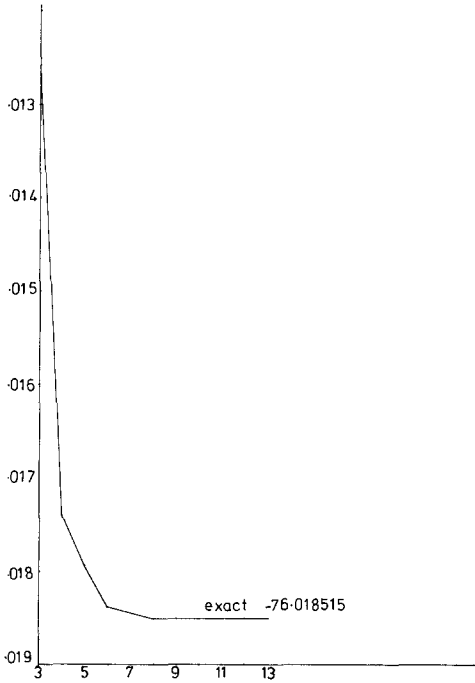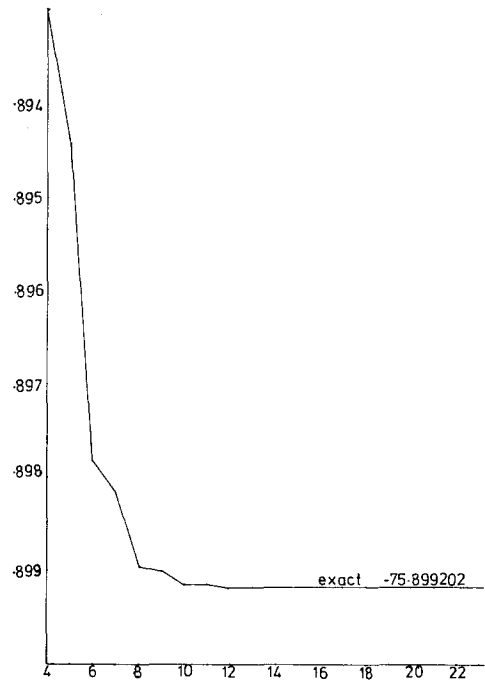
Fig. 1. Convergence of MP-*n* series (RHF)
(H_2O at R_e)

Fig. 2. Convergence of MP-*n* series (RHF)
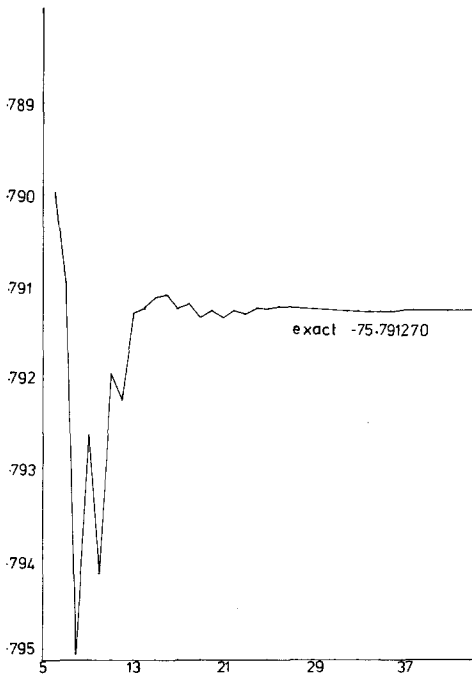(H_2O at $1.5R_e$)

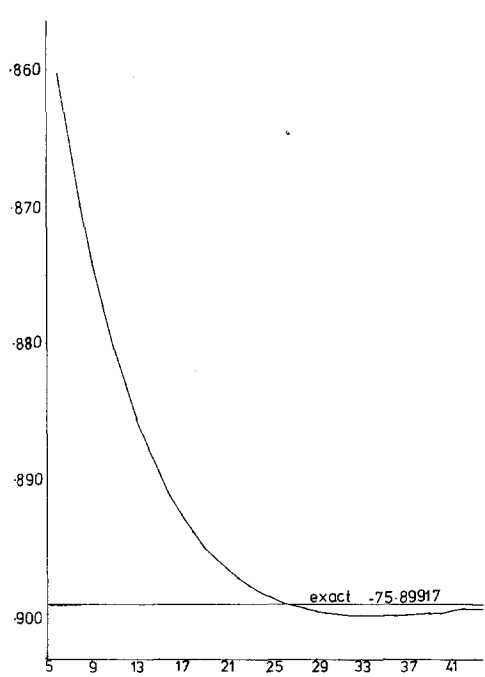**Fig. 3.** Convergence of MP-*n* series (RHF)
(H_2O at $2R_e$)

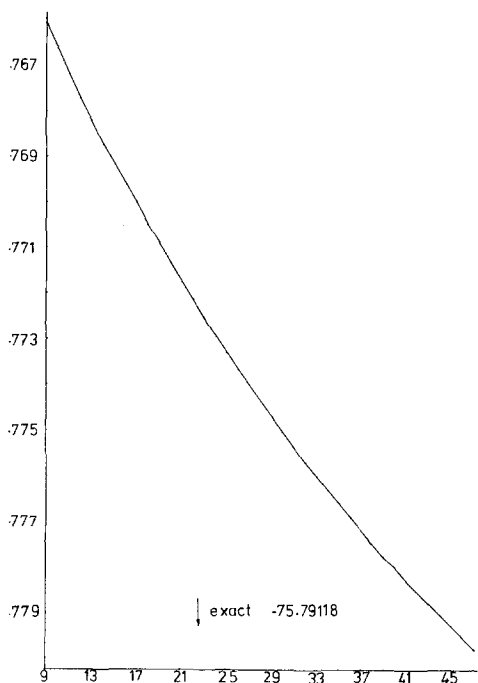**Fig. 4.** Convergence of MP-*n* series (UHF)
(H_2O at $1.5R_e$)
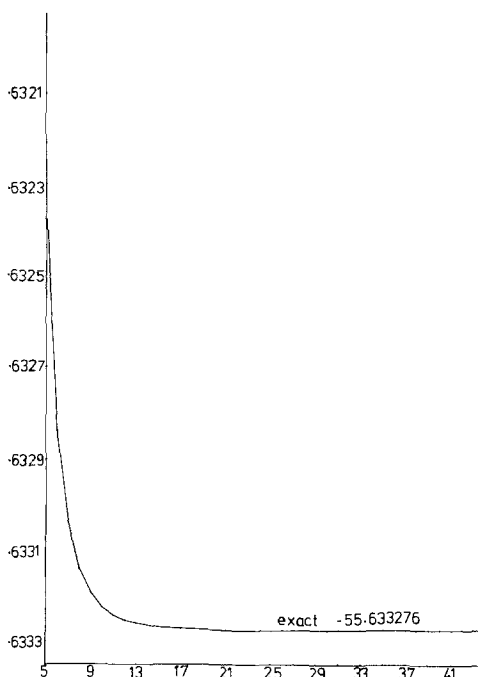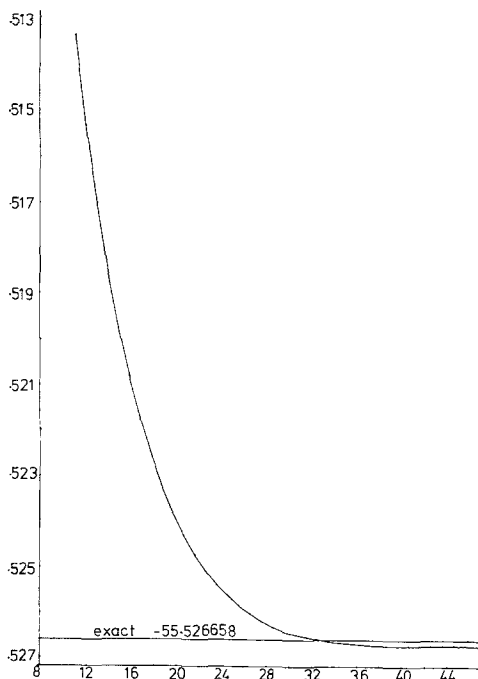
Fig. 5. Convergence of MP-n series (UHF) (H_2O at $2R_e$)

Fig. 6. Convergence of MP-n series (UHF) (NH_2 at R_e)

Fig. 7. Convergence of MP-n series (UHF) (NH_2 at $1.5R_e$)
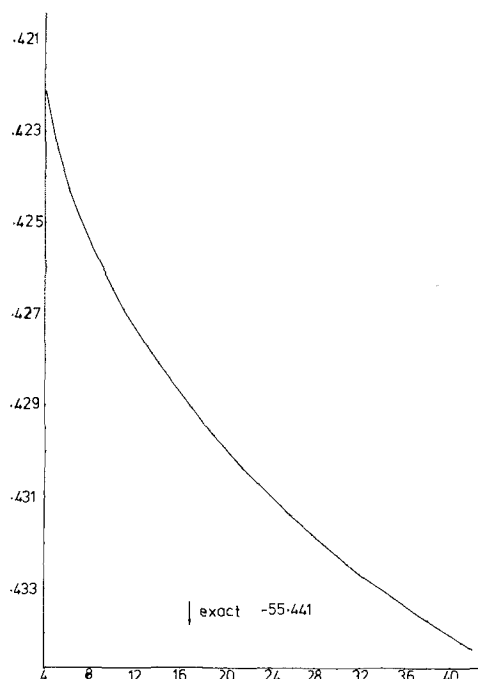

Fig. 8. Convergence of MP-n series (UHF) (NH_2 at $2R_e$)

(ii) H_2O, $1.5r_e$, RHF

This MP series is also strongly convergent, but Fig. 2 shows some disturbance between E_6 and E_9. The numbers of terms after E_0 needed so that the energy is within 10^{-4}, 10^{-5}, 10^{-6} hartree of the exact value are 8, 10, 17. Again the early rapid convergence is not maintained: $E_2/E_4 = 9.86$, $E_4/E_6 = 4.95$, $E_6/E_8 = 4.13$, $E_8/E_{10} = 4.37$.

(iii) H_2O, $2r_e$, RHF

This MP series ultimately converges, as is clear from Fig. 3, but the numbers of terms after E_0 needed so that the accuracy is 10^{-3}, 10^{-4}, 10^{-5} hartree are 7, 13, 24. It is noted that $\sum^8 E_i$ is 0.0037 hartree below the exact eigenvalue. The convergence is highly erratic, but the fact that the MP series converges at all is significant, especially when it is realised that the correlation energy at $2r_e$ (0.30) is 2.3 times that at r_e (0.13). In a full-CI calculation the coefficient of ψ_0 in the CI vector is 0.76, and so this is a good example where ψ_0 cannot be considered dominant.

(iv) H_2O, $1.5r_e$, UHF

The MP series in the UHF framework do not show the irregularities in behaviour of the RHF results. Figures 4–8 all appear smooth. It is significant that although the correlation energy (Exact-SCF) is smaller in the UHF formalism than in the RHF formalism, the convergence is very much slower, as is indicated by the fact that 23 terms are required so that the accuracy is within 10^{-3} hartree. It is also noted from Fig. 4 that the graph passes through a minimum at E_{40}, which is 0.00095 hartree below the exact value. Notice also that the convergence rate gets slower and slower: $E_2/E_4 = 8.29$, $E_4/E_6 = 1.76$, $E_6/E_8 = 1.38$, $E_{11}/E_{14} = 1.30$.

(v) H_2O, $2r_e$, UHF

It is not certain that the MP series will converge; it appears that it will and to achieve 10^{-4} hartree convergence it will need probably more than 200 terms! This is in spite of the fact the correlation energy (0.092) is one third the RHF value (0.299). The convergence rate is obviously terribly slow; $E_2/E_4 = 25.13$, $E_4/E_6 = 2.60$, $E_{10}/E_{12} = 1.08$, $E_{20}/E_{22} = 1.05$, $E_{30}/E_{32} = 1.04$, $E_{40}/E_{42} = 1.04$.

(vi) NH_2, r_e, $1.5r_e$ and $2r_e$, UHF

The NH_2 results are very similar to the H_2O (UHF) results, except that the numbers involved are smaller; for example the UHF correlation energy at $2r_e$ is 0.059 compared to 0.091 for H_2O. On hindsight it is probably reasonable to argue that the similarity between the H_2O and NH_2 results is to be expected because the $1b_2$ and $3a_1$ orbitals are doubly occupied in ψ_0 for both of these molecules.

A principal curiosity of these results is the poor convergence of the UHF MP series at $1.5r_e$ and $2r_e$. To understand further what is happening, it is interesting

to look at the values of the overlap

$$S_{kl} = \frac{\langle \psi_k | \psi_l \rangle}{\langle \psi_k | \psi_k \rangle^{1/2} \langle \psi_l | \psi_l \rangle^{1/2}}. \tag{10}$$

In Table 4, the selected values of these overlaps are given for NH_2 (r_e, UHF) and NH_2 ($2r_e$, UHF). The significant point is that the majority of S_{kl} ($k, l > 4$) are close to unity, for $2r_e$ indicating the successive ψ_k are only slowly changing. It does not appear to be generally known that this happens in perturbation theory at higher orders. For r_e the earlier ψ_k are sufficiently different to give convergence.

Given the overall pattern of the convergence, one might ask whether there are any rational approximations involving the early terms in the series which approximate to the infinite series. Some information on this aspect is given in Table 5. In the first row of the table the correlation energies are given, defined by the (exact eigenvalue — SCF value). In the second row, the approximation suggested by Pople et al. [11] for the series,

$$E_{corr} = (E_2 + E_3)/(1 - E_4/E_2), \tag{11}$$

is given. This approximation is useful at r_e, according to these results, but at distorted geometries, especially for the UHF method, it is poor. At $1.5r_e$ for NH_2, the error is 0.036 hartree. This is particularly disturbing for those who use this extrapolation.

There then follows in the table four Pade approximants $[m, n]$, defined by

$$[m, n] = \frac{a_0 + a_1 \lambda + \cdots + a_n \lambda^n}{1 + b_1 \lambda + \cdots + b_m \lambda^m}, \tag{12}$$

Table 4. Selected values of S_{kl} (Eq. 10) for $NH_2(r_e)$ and $NH_2(2r_e)$

l	$NH_2(r_e)$ $k = 16$	$NH_2(2r_e)$ $k = 16$	$NH_2(r_e)$ $k = 10$	$NH_2(2r_e)$ $k = 10$
2	0.1817	0.5690	0.0848	0.1843
3	0.3481	0.7648	0.2698	0.6198
4	0.5120	0.8541	0.4902	0.8331
5	0.6460	0.9031	0.6855	0.9185
6	0.7416	0.9317	0.8290	0.9599
7	0.8080	0.9506	0.9144	0.9803
8	0.8561	0.9641	0.9615	0.9909
9	0.8931	0.9744	0.9857	0.9965
10	0.9227	0.9822	0.9969	0.9992
11	0.9469	0.9883	1.0000	1.0000
12	0.9663	0.9929	—	—
13	0.9813	0.9962	—	—
14	0.9918	0.9984	—	—
15	0.9980	0.9996	—	—
16	1.0000	1.0000	—	—

Table 5. Rational approximations, for the correlation energy, obtained from the MP perturbation series. Energies relative to the correlation energy are given

	$H_2O(r_e)$ RHF	$H_2O(1.5r_e)$ RHF	$H_2O(2r_e)$ RHF	$H_2O(1.5r_e)$ UHF	$H_2O(2r_e)$ UHF	$NH_2(r_e)$ UHF	$NH_2(1.5r_e)$ UHF	$NH_2(2r_e)$ UHF
E(corr)	-0.130085	-0.191997	-0.299864	-0.16416	-0.09188	-0.101029	-0.121515	-0.059
$(E_2+E_3)/(1-E_4/E_2)$	-0.000728	-0.004024	-0.008274	-0.04838	-0.02843	-0.001498	-0.036041	-0.018
[2, 2]	-0.011050	-0.023331	-0.056053	-0.07994	-0.02725	-0.000127	-0.008649	-0.017
[3, 2]	-0.000536	-0.004778	-0.014021	-0.03975	-0.02709	-0.000314	-0.022173	-0.016
[1, 1]*	-0.016273	-0.018973	-0.058934	-0.08377	-0.03034	-0.000014	-0.011292	-0.017
[2, 1]*	-0.000310	-0.002487	+0.000143	-0.03682	-0.02709	-0.000305	-0.021875	-0.016
MP4	-0.001069	-0.006161	-0.017878	-0.05096	-0.02876	-0.002089	-0.039311	-0.019
MP5	-0.000580	-0.004809	-0.013659	-0.04529	-0.02781	-0.000897	-0.033535	-0.018
MP10	-0.000004	-0.000006	+0.002905	-0.02180	-0.02452	-0.000051	-0.015453	-0.015
MP20	0.000000	0.000000	+0.000006	-0.00326	-0.01982	-0.000001	-0.002783	-0.011
MP30	0.000000	0.000000	-0.000005	+0.00076	-0.01612	0.000000	-0.000180	-0.009
MP40	0.000000	0.000000	0.000000	+0.00074	-0.01314	0.000000	+0.000131	-0.007

the coefficients determined by fitting E_0, E_1, E_2, ..., E_{m+n} to the λ expansion of this. $[m, n]^*$ is the shifted approximant obtained by fitting E_2, E_3, ..., E_{m+n+2} [12].

The $[2, 2]$ (and $[1, 1]^*$) are inferior to MP4, whereas the $[3, 2]$ (and $[2, 1]^*$) are much superior. However the approximation (11) is as good as the $[3, 2]$, in general terms, and is of course much easier to calculate, because it does not rely on E_5. However it must be said that the figures demonstrate why rational approximations will not give chemical accuracy (0.001 hartree) in these energies — the erratic behaviour of the RHF series and the extremely slow convergence of the UHF series away from equilibrium precludes high accuracy rational approximations.

Bartlett and Shavitt [12] have also examined in some detail the Pade approximants to MP series. However in their case they only considered the contributions to E_k from double excitation diagrams, at equilibrium geometry, but with a considerably better basis set. The fact that their series is similar to our Fig. 1 indicates that the convergence patterns presented in this paper would probably be maintained if substantially larger basis sets were used.

That the UHF series is so slowly convergent away from equilibrium is a matter for serious concern. It must be linked to the fact that $\langle S^2 \rangle$ for ψ_0 (for NH_2) at r_e, $1.5r_e$ and $2r_e$ is 0.752, 1.661, 2.51 respectively.

There have also been other systems for which higher order terms in the MP series have been determined. In our earlier publication, we also considered BH, $CH_2(^1A_1)$, Be_2 and Be. The CH_2 and BH calculations, performed at equilibrium geometry, showed the same features as H_2O at r_e, whereas the Be_2 and Be showed a similarity to the UHF NH_2 at r_e, being very smooth, but dipping below the exact value before the ultimate convergence. Laidig et al. [10] also treated Be_2 BH, HF and H_2O, going only as far as E_5 for the last two molecules. Laidig et al. argue that $[2, 1]^*$ may be a useful approximation if E_5 is known, but our results on NH_2 and H_2O in the UHF approximation show that it can also be poor. We also observe that all higher perturbation energies E_k can be positive or negative.

In summary we may try to answer the questions posed in the introduction.

(a) Evidence from these results is that the MP series will converge for most molecular calculations. Even at our distorted geometries, the series appear ultimately to converge.

(b) At equilibrium geometries of the well behaved molecules we have considered, the MP series is rapidly convergent. Away from equilibrium, the RHF series are erratic and the UHF series are smooth but very slowly convergent.

(c) At equilibrium, the formula (11) appears to be better than the corresponding Pade approximant, and, in our limited experience, will be useful. However away from equilibrium, the value of such approximations must become limited, as is demonstrated for the UHF calculations at $1.5r_e$.

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