

THE CALCULATION OF HIGHER-ORDER ENERGIES IN THE MANY-BODY PERTURBATION THEORY SERIES

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Perturbation energies through 8th order, have been calculated for the molecules H_2O , CH_2 , BH and Be_2 using a variety of basis sets. The purpose of these calculations is to examine the errors involved in the usual truncation of the series at 4th or lower order as in standard many-body perturbation theory or Møller–Plesset calculations. Conclusions appear to be that the series are convergent, but that successive error terms do not reduce in size particularly rapidly.

1. Introduction

Nowadays, many thousands of quantum chemistry calculations are performed on small and medium-sized molecules within the framework of perturbation theory. Such programs have become standard tools for many research workers through the availability of programs such as the GAUSSIAN packages (developed by Pople and co-workers [1,2]) and others. Pople and co-workers work in the framework of the restricted Hartree–Fock (RHF) scheme for closed-shell systems and unrestricted Hartree–Fock (UHF) for open-shell systems, and use Møller–Plesset (MP) perturbation theory [3,4] to calculate estimates for the electron correlation energy. The latest programs calculate the perturbation series energies E_0, E_1, E_2, E_3, E_4 , where for example the sum of these through E_4 is referred to as the MP4 energy for the system.

An alternative formulation of the problem is through many-body perturbation theory (MBPT) [5]. This theory, which is usually discussed in terms of diagrams, leads to the same perturbation energies E_i , within the framework of RHF and UHF discussed above. Such calculations are often referred to in the literature as MBPT(4) to denote the sum of the per-

turbation energies through 4th order.

Workers have not extended their programs beyond 4th order, because of the substantial amounts of computer time which would be needed to evaluate 5th and 6th order formulae, let alone the complexity of programming the formulae. It may simply be shown that the calculation of E_m is an $N^{2(m-1)}$ process, where N is the number of orbitals involved.

The purpose of this paper is to examine the convergence of the perturbation series, that is to examine the rapidity of its convergence and to discuss the errors involved by the truncation of the series at 4th order. We shall also discuss the continuation of such series with Padé approximants. As we see it, the only way to carry out such an investigation is to perform calculations on as many molecules as possible using a variety of basis sets, allowing those basis sets to be as large as possible. Some investigations using very small systems or very small basis sets have already been published [6].

Fortunately we now have available a fully vectorised full (or complete) CI program which needed only minor adaptation to evaluate successive perturbation energies. This CI program uses as expansion functions single Slater determinants; its efficiency and its appli-

cation to other problems have been described elsewhere [7,8]. In section 2 the theory of the approach is introduced; in section 3 the results are presented and in section 4 they are analysed and discussed.

2. Method

Given a zeroth-order Hamiltonian H_0 , the zeroth-order Schrödinger equation is

$$H_0\psi_0 = E_0\psi_0, \quad (1)$$

and the k th equation is

$$(H_0 - E_0)\psi_k + (H_1 - E_1)\psi_{k-1} - \sum_{r=2}^k E_r \psi_{k-r} = 0, \quad (2)$$

with the Hamiltonian H being given by

$$H = H_0 + H_1. \quad (3)$$

Intermediate normalisation $\langle \psi_0 | \psi_k \rangle = 0$ ($k > 0$), is used. Since direct CI programs evaluate residual vectors σ , e.g.

$$\sigma_k = H\psi_{k-1}, \quad (4)$$

one may get E_k and ψ_k with the aid of σ_k as

$$E_k = \langle \psi_0 | \sigma_k \rangle, \quad (5)$$

$$\psi_k = (H_0 - E_0)^{-1} \left(\sum_{r=1}^k E_r \psi_{k-r} + H_0 \psi_{k-1} - \sigma_k \right), \quad (6)$$

which follows immediately from eq. (2). The connection to MBPT and the evaluation of (5) and (6) is straightforward if $H_0 = F$, the n -particle Fock operator, and if one works in the molecular orbital basis of Fock orbitals, since H_0 is then diagonal in the basis of n -particle Slater determinants.

There are of course other ways of calculating the energies E_k , such as fitting variationally calculated energies $E(\lambda)$, determined for different values of the parameter λ , to a polynomial in λ . But we believe that probably the above method represents the most simple and numerically stable approach.

In summary, to calculate the k th perturbation energy needs computation time equivalent to k iterations of our standard full CI program. The examples in the next section are given for closed-shell systems, and later we shall present a fuller set of results which will include some for open-shell systems based on the UHF formalism.

3. The calculations

The following systems were investigated:

(a) $\text{H}_2\text{O}(^1\text{A}_1)$. The calculations were carried out using a split valence 6-21G basis set [9] with a frozen core at selected geometries,

(i) $R = 0.967 \text{ \AA}$ ($= r_e$) and $\alpha = 107.6^\circ$,

(ii) $R = 1.450 \text{ \AA}$ ($= 1.5r_e$) and $\alpha = 107.6^\circ$,

(iii) $R = 1.933 \text{ \AA}$ ($= 2.0r_e$) and $\alpha = 107.6^\circ$.

The number of determinants used in these full CI calculations was 61441.

(b) $\text{BH}(^1\Sigma_g^+)$. The basis set used was an 8s, 4p, 1d set of uncontracted Gaussians on boron and a 4s, 1p set on hydrogen. The s and p functions of boron and the s functions of hydrogen are taken from ref. [10]. The d-exponent of boron and the p-exponent of hydrogen were taken from ref. [11]. Core electrons on boron were frozen and the highest virtual orbital was excluded. The bond length was taken as 1.235 Å. The number of determinants used in the full CI calculation was 53693.

(c) $\text{CH}_2(^1\text{A}_1)$. Calculations used the double-zeta plus polarization functions on carbon and double-zeta on hydrogen [12] (the d function exponent on carbon was taken as 0.8) with the bond length 1.102 Å and the bond angle 104.7° . The number of determinants was 116292.

(d) $\text{Be}_2(^1\Sigma_g^+)$. Calculations used the 7s, 3p, 1d basis of van Duijneveldt [10] with two frozen core orbitals and the highest two virtual orbitals excluded, at various internuclear distances $R = 4.5, 4.75, 5.0, 5.25, 6.5, 8.0, 8.5, 9.5, 11.0$ and 20.0 bohr. The 7s, 3p functions were obtained from 12s, 6p functions [10] by contracting the inner 6s and 4p functions. Six components of d functions were used. The number of determinants was 84368.

(e) $\text{Be}(^1\text{S})$. Two different calculations used (i) the 9s, 5p, 3d, 1f basis and (ii) the 7s, 3p, 1d basis of van Duijneveldt [10] with the frozen core and the highest virtual orbital excluded. The exponents for the d and f functions of basis (i), which were uncontracted, were 1.00, 0.35, 0.10, 0.30, and the exponent of the d function for basis (ii) was 0.20. The numbers of determinants for calculations (i) and (ii) were 344 and 94 respectively.

4. Discussion

The first observation from tables 1 and 2, where the perturbation energies are shown, is that it is difficult to make comments which apply to all the molecules. The degree of convergence of the series to the variational energy E_v , and the size of the individual terms vary for each of the molecules. However from this selected set of results the following appears:

(a) $|E_4| > |E_v - \Sigma^4 E_i|$.

(b) $|E_6| > |E_v - \Sigma^6 E_i|$.

(c) The rapidity of convergence decreases significantly in the higher-order terms of the series.

(d) The results for H_2O , at $2r_e$ indicate that the

odd members of the perturbation series converge in a different way to the even members.

These results may be criticised because the molecules are too small. But we observe that CH_2 has six electrons and 19 basis functions were used, and for Be_2 (albeit only four electrons), 42 basis functions were used. Our view is that there is a sufficient variety of results here from which to draw the above conclusions, which will probably hold to some degree for the majority of molecular calculations considered by most workers.

We have been unsuccessful in finding any Padé approximant which is appropriate for the series, indeed the conclusion under (d) and (c) above indicates that

Table 1
Perturbation energies in hartree for small molecules with various basis sets

Molecule	E_0	E_1	E_2	E_3	E_4
H_2O r_e	-58.226579	-17.661851	-0.120865	-0.003303	-0.004849
1.5 r_e	-59.833618	-15.373588	-0.166896	-0.002015	-0.016925
2.0 r_e	-60.701577	-14.789829	-0.241643	+0.006123	-0.046465
BH	-22.682854	-2.441712	-0.065007	-0.017081	-0.006113
CH_2	-31.924104	-6.952254	-0.092657	-0.017926	-0.005476
Be (i)	-14.229393	-0.343237	-0.028910	-0.008590	-0.004174
(ii)	-14.229689	-0.343241	-0.026874	-0.010015	-0.004467
	E_5	E_6	E_7	E_8	E_9
H_2O r_e	-0.000488	-0.000435	-0.000076	-0.000048	-0.000012
1.5 r_e	-0.001352	-0.003417	-0.000339	-0.000827	-0.000032
2.0 r_e	-0.004219	-0.012369	-0.001032	-0.004065	+0.002319
BH	-0.002568	-0.001231	-0.000634	-0.000337	-0.000180
CH_2	-0.002018	-0.000973	-0.000567	-0.000373	-0.000264
Be (i)	-0.002209	-0.001144	-0.000563	-0.000255	-0.000100
(ii)	-0.002203	-0.001103	-0.000527	-0.000229	-0.000082
	E_{10}	$\Sigma_i^{10} E_i$	E_v^a		
H_2O r_e	-0.000006	-76.018512	-76.018515		
1.5 r_e	-0.000189	-75.899196	-75.899202		
2.0 r_e	-0.001417	-75.794175	-75.791269		
BH	-0.000095	-25.217813	-25.217904		
CH_2	-0.000195	-38.996808	-38.997538		
Be (i)	-0.000028	-14.618603	-14.618562		
(ii)	-0.000017	-14.618447	-14.618397		

a) The variational energy.

Table 2
 Perturbation energies in hartree for Be_2 , using a $7s, 3p, 1d$ basis at various internuclear distances

R	E_0	E_1	E_2	E_3	E_4	E_5
4.50	-27.616106	-1.515561	-0.065754	-0.021396	-0.009749	-0.004610
4.75	-27.652960	-1.482018	-0.063999	-0.021131	-0.009487	-0.004464
5.00	-27.687033	-1.450255	-0.062439	-0.020925	-0.009277	-0.004357
5.25	-27.718726	-1.420254	-0.061087	-0.020766	-0.009116	-0.004283
5.50	-27.748319	-1.391963	-0.059934	-0.020642	-0.009001	-0.004238
6.50	-27.849174	-1.294279	-0.056863	-0.020358	-0.008839	-0.004226
8.00	-27.960205	-1.185086	-0.054864	-0.020173	-0.008869	-0.004314
8.50	-27.989225	-1.156301	-0.054545	-0.020137	-0.008883	-0.004338
9.50	-28.038438	-1.107315	-0.054165	-0.020090	-0.008904	-0.004367
11.0	-28.095748	-1.050090	-0.053917	-0.020056	-0.008920	-0.004389
20.0	-28.259378	-0.886483	-0.053750	-0.020032	-0.008934	-0.004406
∞	-28.459378	-0.686483	-0.053748	-0.020031	-0.008933	-0.004407
	E_6	E_7	E_8	$\sum_i^8 E_i$	E_v	BE ^{a)} (kcal/mo ³)
4.5	-0.002303	-0.001081	-0.000464	-29.237023	-29.236982	0.1173
4.75	-0.002219	-0.001041	-0.000452	-29.237772	-29.237793	0.6262
5.00	-0.002154	-0.001008	-0.000439	-29.237887	-29.237947	0.7229
5.25	-0.002107	-0.000984	-0.000429	-29.237753	-29.237835	0.6526
5.50	-0.002078	-0.000970	-0.000421	-29.237565	-29.237659	0.5422
6.50	-0.002071	-0.000973	-0.000421	-29.237204	-29.237313	0.3250
8.00	-0.002139	-0.001017	-0.000441	-29.237111	-29.237219	0.2661
8.50	-0.002156	-0.001026	-0.000445	-29.237057	-29.237163	0.2309
9.50	-0.002177	-0.001038	-0.000450	-29.236943	-29.237047	0.1581
11.0	-0.002193	-0.001047	-0.000454	-29.236819	-29.236920	0.0784
20.0	-0.002205	-0.001054	-0.000457	-29.236699	-29.236798	0.0019
∞	-0.002206	-0.001054	-0.000457	-29.236697	-29.236795	0.0

a) Binding energy.

any approximant based on the first five terms in the series will be rather poor.

The results for Be_2 are interesting. In agreement with the results of Lee and Bartlett [13], the MBPT(4) binding energy is 0.001386 hartree and the full CI binding energy is 0.00112 hartree. Of course these results are inferior to best results [14] because of the inadequacy of the basis set. The variation of the higher-order perturbation energies with internuclear distance is minimal, for example E_6 varies by 0.0001 hartree over the range 5 bohr to dissociation.

There is a very interesting aspect of the $1.5r_e$ and $2r_e$ calculations on H_2O , the 4.50 calculation on Be_2 and the calculations of Be; for example, for type (ii) calculations on Be E_i is lower than E_v by 0.000049 hartree and for $\text{H}_2\text{O}(2r_e)$ E_i is lower than E_v by 0.002906 hartree. This means that some of the higher

E_i must be positive, indeed for H_2O it is seen that E_9 is positive.

In conclusion the results of this short paper lend support to those who carry out MBPT(4) or MP4 calculations, in so far as E_4 appears to be larger than the sum of all the remaining terms in the perturbation series. However we have shown that there is no overall pattern to the convergence of the series, other than the convergence becoming slower as a larger number of terms is taken. Furthermore, it is well known that where the zeroth-order wavefunction is a poor approximation, for example when there are near degeneracies and in many molecular dissociations, the convergence of the perturbation series is much inferior to the simple examples we have been able to investigate.

Finally we remark that, because we work with Slater determinants rather than spin eigenfunctions,

investigation of the perturbation series based on a spin unrestricted Hartree-Fock wavefunction is entirely straightforward, and we plan to consider such series in a future publication.

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References

- [1] J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, QCPE 13 (1981) 406.
- [2] J.S. Binkley, M.J. Frisch, D.J. DeFrees, R. Krishnan, R.A. Whiteside, R. Seeger, H.B. Schlegel and J.A. Pople, GAUSSIAN-82, Carnegie-Mellon University, Pittsburgh, PA.
- [3] C. Møller and M.S. Plesset, *Phys. Rev.* **46** (1934) 618.
- [4] J.S. Binkley and J.A. Pople, *Intern. J. Quantum Chem.* **9** (1975) 229.
- [5] S. Wilson, *Specialist Periodical Reports, Theoretical Chemistry Vol. 4* (Chem. Soc, London, 1981) p. 1; R. J. Bartlett, H. Sekino and G. D. Purvis, *Chem. Phys. Letters* **98** (1983) 66.
- [6] J. Paldus, J. Čížek and I. Shavitt, *Phys. Rev. A* **5** (1972) 50; K. Jankowski and J. Paldus, *Intern. J. Quantum Chem.* **18** (1980) 1243.
- [7] P.J. Knowles and N.C. Handy, *Chem. Phys. Letters* **111** (1984) 315.
- [8] P.J. Knowles and H.-J. Werner, to be published.
- [9] J.S. Binkley, J.A. Pople and W.J. Hehre, *J. Am. Chem. Soc.* **102** (1980) 939.
- [10] F.B. van Duijneveldt, IBM Res. Report RJ 945 (No. 16437).
- [11] J.A. Pople, J.S. Binkley and R. Seeger, *Intern. J. Quantum Chem.* **S10** (1976) 1.
- [12] T.H. Dunning, *J. Chem. Phys.* **53** (1970) 2823.
- [13] Y.S. Lee and R.J. Bartlett, *J. Chem. Phys.* **80** (1984) 4371.
- [14] B.H. Lengsfeld, A.D. Mclean, M. Yoshimine and B. Liu, *J. Chem. Phys.* **79** (1983) 1891.