Full CI Extrapolation: Application to H_2O with a Double Zeta Basis Set*

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Abstract

A previously reported full CI (configuration interaction) extrapolation procedure based on multi-reference single and double CI, which gave excellent results for H_2O at the equilibrium geometry, is extended to two other geometries for which explicit full CI results are known. The technique is shown to provide good results for cases where the SCF (self-consistent field) configuration is not strongly dominant, although degradation of performance is noticeable in these cases. The technique is also used to predict a full CI result for the 2^1A_1 state of H_2O with the double zeta basis.

1. Introduction

Although there are many methodologies available for the computation of molecular electronic energy states (Shavitt 1984), the MRDCI (multi-reference double configuration interaction) method is valuable in that it allows direct control over the size and accuracy of the calculation and systematic determination of the error in the final computed energies. The control over the accuracy of the calculation (assuming the atomic basis functions remain unchanged) is accomplished by (i) varying the configuration selection threshold T to reject any configurations which interact with the reference state(s) with an energy less than T and (ii) varying the number and type of the root (reference) or parent (generating) configurations to control the configuration subspace from which the configurations used in the final CI are selected.

Our interest in the control of errors in an energy calculation is driven by the possibility of extrapolating the results of several calculations of increasing size to the zero error (full CI) level. The possibility of full CI extrapolation was first explored for the H_2–H_2 interaction problem (Burton 1983*a*, 1983*b*) (in advance of the full CI being known) and later tested on the BH molecule (Burton *et al.* 1983) for which the exact full CI result was known (Harrison and Handy 1983). The results for BH were successful enough to warrant further testing of the technique on the H_2O molecule (Burton and Gray 1983) which had earlier been the subject of an explicit full CI calculation (Saxe *et al.* 1981; Harrison and Handy 1983). These results indicated that the full CI extrapolation technique significantly reduced errors in MRDCI results while still keeping the size of the final CI manageable. Perhaps even more importantly,

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both the internal consistency and systematic improvement of calculations forming the basis of the extrapolation become directly visualised through the extrapolation graphs; both precision and accuracy (with respect to full CI energies) are thus objectively presented. This facilitates independent assessment of the quality of the calculation in absolute terms for a given basis set, in the normal case where the full CI energy is unknown.

Subsequent work by Phillips et al. (1984) on H_2O with a double zeta basis indicated that the extrapolation technique might not produce reliable results for H_2O at other than the equilibrium geometry. This would imply that the extrapolation procedure only worked satisfactorily in cases where the SCF (self-consistent field) configuration is strongly dominant. The formula for determining the error estimate used as the basis of the extrapolation is in fact formulated for a dominant SCF situation, since the formula is aimed at estimating dynamic correlation errors. Any important degeneracy effects (non-dynamic correlation) need to be addressed independently by Main selection or an explicit MCSCF (multi-configuration self-consistent field) step. The study by Phillips et al. of the three H_2O geometries raised the problem of designing reliable extrapolation strategies for cases where the SCF configuration is not strongly dominant. The question we seek to answer in the present paper is whether the configuration selection strategy can be made sufficiently general to circumvent the need for an MCSCF step as the basis of the extrapolation procedure. This question pivots on the appropriate selection strategies to ensure all non-dynamically important configurations are included in the reference CI, before the dynamic correlation based extrapolation can be relied upon to yield the apparently linear approach to the full CI limit.

2. Methodology

The basis of the extrapolation procedure is a plot of the variational MRDCI energies against an estimate of the total error in the calculation as the error estimate is reduced by considering successively larger CI subspaces by inclusion of more Main or parent configurations. The new Main configurations for each successive calculation in a series are selected from the most 'important' generated configurations in the current calculation. Exactly how the importance of a generated configuration is assessed may vary depending on the nature of the calculation. We have tested two methods: (i) second order perturbation theory interaction energies with the reference state(s) and (ii) the magnitude of each configuration's coefficient in the CI eigenvector(s).

The error estimate used as the abscissa in the extrapolation (ΔE_2) was obtained from the formula (Siegbahn 1978; Wilson 1981; Paldus et al. 1982; Burton et al. 1983)

$$\Delta E_2 = (1 - 2N^{-1})\{(1 - C_R^2)/C_R^2\}(E_{MRDCI}^m - E_{ref}^m),$$

where E_{MRDCI}^m is the variational MRDCI energy computed from a CI with m Main configurations, E_{ref}^m is the energy obtained from the $m \times m$ CI used to define the reference state(s), N is the number of electrons in the system and C_R^2 is the accumulated weight of the m parent configurations in the m Main subspace CI.

This error estimate formula reflects an attempt to correct for the error due to omission of configurations which are unlinked or disconnected clusters of the included configurations. Thus the error estimate is not meant to give an inclusive representation of the error in the calculation (compared with the full CI result) but is used in

the anticipation that, for sufficiently large numbers of Mains, it will give a constant proportion of the total error. Should this occur, the extrapolation graph will be linear and extrapolate to the full CI result. This behaviour has been observed in several instances but can only be expected when the Main selection and m Main single and double excitation subspace computation already include a dominant part of the correlation energy accessible with the AO (atomic orbital) basis, and dynamic correlation refinements are the dominant residual correction to be made.

3. Results

Analysis of the work by Phillips *et al.* (1984) on H_2O at other than the equilibrium geometry showed that Main configuration selection by second order perturbation theory energy of interaction with the reference state did not guarantee a significant decrease in the ΔE_2 between adjacent calculations. This leads to 'bunching up' of successive m Main MRSDCI (multi-reference single and double CI) selected subspace energies so that extrapolation towards full CI becomes very uncertain.
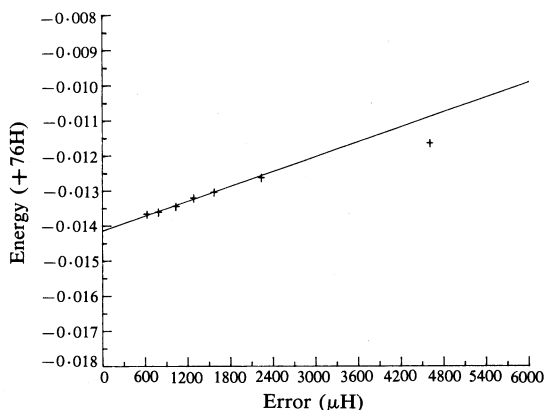

Fig. 1. The MRSDCI results for the 1^1A_1 state of H_2O at $1 \cdot 5 R_e$ with 5, 15, 20, 27, 32, 38, 46 and 52 Main configurations. The coefficient selection thresholds used to obtain this Main series were $0 \cdot 1$, $0 \cdot 04$, $0 \cdot 03$, $0 \cdot 025$, $0 \cdot 022$, $0 \cdot 020$, $0 \cdot 019$ and $0 \cdot 016$ respectively. The extrapolation uses the last four points and produces a full CI estimate of $-76 \cdot 014141$ H for our gaussian lobe basis set or $-76 \cdot 014105$ H for a cartesian gaussian basis set (H, hartree units; $1\,H = 3 \cdot 808 \times 10^{-4}\,kJ\,mol^{-1}$).

To overcome this problem we investigated a systematic alternative to Main selection based on the coefficient of configurations in the CI eigenvector. Selection of Mains in this manner directly increases the C_R^2 value as new Mains are added thus ensuring a decrease in ΔE_2 between successive calculations. A large coefficient of a trial configuration reduces the $(1 - C_R^2)/C_R^2$ component of the error and is normally also accompanied by a significant lowering in E_{ref}^m, which reduces the last multiplicative component of the error. Furthermore, selection of Mains in this manner raises the possibility of extrapolation for excited states of a given symmetry since new Mains may be chosen by coefficient from any of the CI vectors. Figs 1 and 2 show the
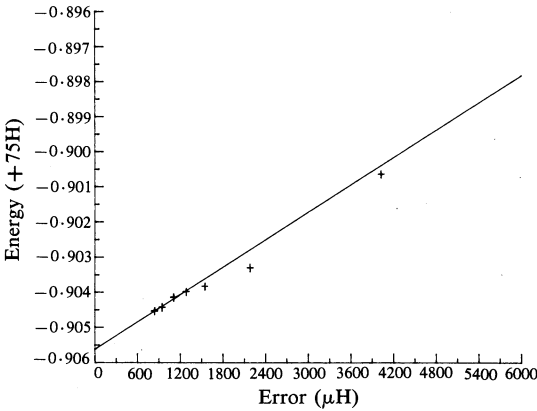
Fig. 2. The MRSDCI results for the $1\,{}^1A_1$ state of H_2O at $2 \cdot 0 R_e$ with 7, 13, 22, 28, 33, 38, 45 and 50 Main configurations. The extrapolation uses the last four points and produces a full CI estimate of $-75 \cdot 905629$ H for the gaussian lobe basis set or $-75 \cdot 905609$ H for a cartesian gaussian basis set.

Table 1. Summary of results for the $1\,{}^1A_1$ state of H_2O obtained by the present extrapolation procedure, and comparison with recent CASSCF and CI results

SAF, spin symmetry adapted function

	Active space	R_e	$1 \cdot 5 R_e$	$2 \cdot 0 R_e$	SAF (256473)
			Error (μH w.r.t. full CI)		
		CASSCF[A]			
	7	92765	87263	76831	(70)
	8	58466	58591	59576	(328)
	9	25220	32469	39092	(1436)
		CASSCF/MRSDCI[A]			
	7	1936	2057	1898	(7906)
	8	377	489	539	(22644)
	9	76	172	142	(52452)
		Subspaces of full CI			
SD[A]		7851	22381	60430	(361)
SDT[A]		6710	18678	49720	(3203)
SDTQ[A]		263	1103	4351	(17678)
SD+DC[A]		1954	2654	373	(361)
		Full CI extrapolation			
		+190[B]	+510[B]	−2420[B]	(∼14000)[B]
		−37[C]	+416[C]	−362[C]	(∼14000)[C]
		(−8 cm^{-1})	(+91 cm^{-1})	(−79 cm^{-1})	(∼5% full CI)

[A] Results from Brown *et al.* (1984) using a cartesian gaussian basis set. Abbreviations are: CASSCF, complete active space MCSCF; S, all single excitations; SD, S + all double excitations; SDT, SD + all triple excitations; SDTQ, SDT + all quadruple excitations; DC, Davidson correction.
[B] Results from Phillips *et al.* (1984), using spin symmetry adapted functions; comments in their paper relating to previous work (Burton and Gray 1983) are unfounded and relate to an incorrect attribution of basis set effects. The confusion arose in comparison of SAF results and spin complemented determinant (SCD) results for a multiple open shell reference CI. Since the basis set used in the present work employs lobe rather than cartesian functions, the raw extrapolated results have been corrected by +41, +36 and +20 μH for the $1 \cdot 0 R_e$, $1 \cdot 5 R_e$ and $2 \cdot 0 R_e$ cases respectively to be compatible with the cartesian gaussian full CI results.
[C] Present work using a gaussian lobe basis set and spin complemented determinants.

results of extrapolations for H_2O at $1 \cdot 5 R_e$ and $2 \cdot 0 R_e$ respectively based on Main selection by coefficient from the ground state CI vector. Clearly the extrapolation deteriorates as the SCF configuration becomes less dominant, although the near-linear behaviour indicates that it is quite possible to achieve reliable results at other than the equilibrium geometry. Degradation of the extrapolation results at longer bond distances may be expected for H_2O since the SCF determinant becomes less dominant at these geometries. Table 1 shows a summary of the results obtained from the extrapolation procedure as well as a comparison with recent CASSCF and CI results (Brown *et al.* 1984) and the results of Phillips *et al.* (1984) using a purely perturbation theory based Main selection strategy.

As can be seen the error from the full CI extrapolation technique is competitive with CASSCF/MRSDCI results, although requiring much smaller CIs. Even if 100–150 Mains were required to obtain a reliable extrapolation, this still only requires in CIs $\sim 10\%$ of the full CI space resulting in substantial savings in computer resources.
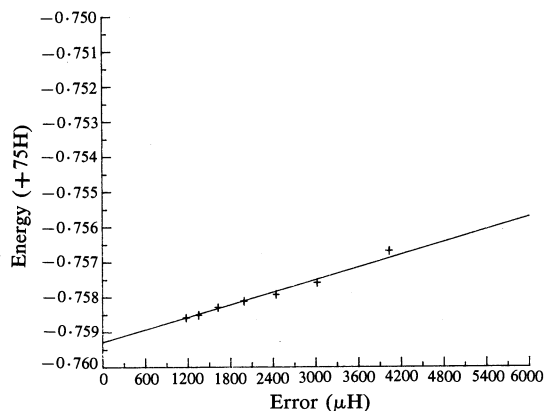

Fig. 3. The MRSDCI results for the 2^1A_1 state of H_2O at $1 \cdot 0 R_e$ with 17, 23, 28, 33, 39, 45 and 50 Main configurations. The extrapolation uses the last four points and produces a full CI estimate of $-76 \cdot 759197$ H for our gaussian lobe basis set.

4. Conclusions

The success of the extrapolation procedure in the cases where the SCF configuration is not extremely dominant led to the possibility of applying the method to excited states of a given symmetry of molecules. Fig. 3 shows the result of the extrapolation for the second state of H_2O with $^1A_1$ symmetry. We note that this result is not physically realistic since only a limited double zeta basis has been used and only the ground state R_e geometry was considered. The Mains used for the extrapolation were selected by coefficient from the lowest two states in an attempt to ensure an even-handed description of both states. Specifically, each new Main is selected on the basis of it having the next largest coefficient in any of the i reference states for which explicit CIs are available. This extrapolation leads to the prediction of $-75 \cdot 759287$ H as the full CI energy for the 2^1A_1 state with this basis set or a vertical transition energy for $2^1A_1 \leftarrow 1^1A_1$ of $10 \cdot 845 \pm 0 \cdot 005$ eV. It is hoped that this prediction can soon be tested against an explicit full CI.

The success of extrapolation procedures for the energy expectation value in a MRDCI calculation leads directly to the possibility of applying similar techniques to properties. Also, it may be important to monitor the convergence of the CI properties while performing the energy extrapolation to ensure quantitative convergence of the wavefunction.

While the success of the extrapolation for H_2O with a very small basis set is encouraging, the question remains as to whether it is possible to obtain similar results for systems with larger basis sets [the H_2–H_2 full CI extrapolation (Burton 1983a) with ~ 80 basis functions has recently been re-investigated in comparison with established MCSCF-CI methodologies (Shavitt et $al.$ 1986)] and more electrons. For a system such as O_3 with, say, 69 basis functions (Burton 1979) and 24 electrons, where the total number of electronic configurations is greater than 10^{12}, it can only be hoped that the full CI extrapolation technique is a viable solution to the brute-force alternative.

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