

Convergence of Projected Unrestricted Hartree-Fock Møller-Plesset Series

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The problem of spin contamination in the unrestricted Hartree-Fock Møller-Plesset (UMP) series is examined, using our full CI programs to generate the series to high order. A scheme involving spin projection of the MP series wave functions has been devised, which shows a substantial improvement over the regular UMP series. Practical schemes for implementing reasonable approximations to the scheme are discussed. It is shown that it is possible to perform a projected second-order calculation at little extra cost, but with substantially better results in cases where spin contamination is severe.

Introduction

The unrestricted self-consistent field (UHF) method¹ is used regularly by quantum chemists in molecular structure calculations. For closed-shell molecules, often the UHF wave function becomes a restricted Hartree-Fock (RHF) wave function, but away from equilibrium geometry the UHF energy is lower than the RHF energy. The principal criticism of UHF theory is that the wave function is not an eigenfunction of \hat{S}^2 , and this has long been recognized as the spin contamination problem. As a measure of this contamination, it is useful to examine $\langle \psi | \hat{S}^2 | \psi \rangle$, where $|\psi\rangle$ denotes the UHF wave function. Perturbation theory is the simplest way to introduce electron correlation into the wave function it is often said, although of course a UHF wave function contains some electron correlation effects because of the different orbitals for different spins concept. Nevertheless, perturbation theory is applied to the UHF wave function, and nowadays it is often referred to as unrestricted Møller-Plesset (UMP) theory.²

In the past we have examined³ the convergence of the Møller-Plesset series for both the restricted (RMP) and unrestricted (UMP) cases. This was possible because of the availability of our efficient program⁴ for full CI calculations. We are able to perform full CI calculations using double ζ size basis sets for small molecules, although more recently, the availability of the CRAY-2 with its very large main memory has considerably increased the size of full CI calculations which may be carried out.⁵

The RMP and UMP series showed some interesting characteristics; we briefly discuss these for H₂O (double ζ basis), C_{2v} symmetry, for the bond lengths R_e , $1.5R_e$, and $2R_e$. At R_e , UHF is equivalent to RHF, and the MP series was rapidly convergent. At $1.5R_e$, the RHF series was slightly erratic, but had converged to within 0.001 hartree by RMP-7, whereas the UMP series was smooth, but slowly convergent, and converges within 0.001 hartree by UMP-23. At $2R_e$, the RHF series was highly erratic up to RMP-10, but after that stage it rapidly converges, whereas at UMP-48, the energy is in error by 0.01 hartree, even though the series is smooth, and the UHF energy is 0.20 hartree lower than the RHF energy. Furthermore, the error in the UMP-4 energies at R_e , $1.5R_e$, and $2R_e$ are 0.001, 0.031, and 0.028 hartree, compared to 0.001, 0.006, and 0.018 hartree for RMP-4. This demonstrates the very unsatisfactory behavior of UMP near $1.5R_e$.

Recently a comment on this problem has been made by established scientists who regularly use the UMP method. Gill and Radom⁶ have studied He₂²⁺ to conclude that, for a closed-shell singlet system, "incorrect dissociation of RHF does not impede the rapid convergence of the MP series as much as spin contamination in the UHF wavefunction does".

We also argued that this very slow convergence of the UMP series is a reflection of the spin contamination referred to earlier. For H₂O at $1.5R_e$ and $2R_e$, $\langle \hat{S}^2 \rangle_{\text{UHF}} = 0.92$ and 1.79 , respectively. In simple terms, it may be that the UMP series wave functions are very slowly converging toward an exact eigenfunction of \hat{S}^2 . It is the purpose of this paper to examine this problem further.

Any good perturbation theory is built upon a well chosen and unambiguous \hat{H}_0 . In MP theory, \hat{H}_0 obeys these strictures, and is $\sum_i^\alpha F^\alpha(i) + \sum_i^\beta F^\beta(i)$, and furthermore, the eigenfunction of \hat{H}_0 is the single determinant ψ_0 . Unfortunately we, in common with many others, cannot devise such a \hat{H}_0 for general open-shell systems for which ψ_0 has a simple form and is an eigenfunction of \hat{S}^2 . It is possible, using appropriate projection operators, to devise a form for \hat{H}_0 for open-shell (high spin) systems, as shown by Hubač and Čarský,⁷ but the form of \hat{H}_0 is difficult to attribute useful meaning. Schlegel⁸ observes that perturbation theory for open-shell systems based on this \hat{H}_0 is slow to converge when occupied and unoccupied orbitals are nearly degenerate.

An alternative procedure is to work with the wave function $\hat{O}\psi$, where \hat{O} is the Löwdin spin projection operator⁹ and ψ is a single determinant. The spin extended Hartree-Fock method¹⁰ optimizes the parameters in the wave function by the variational method, but the procedure is complicated, and it is difficult to devise a perturbation theory built on this method.⁸

Accepting this position, one way to proceed is to use the UMP wave function series in combination with the Löwdin spin projection operator; spin projection for UHF wave functions was first suggested by Amos and Hall.¹¹ Recently, Schlegel⁸ has attempted this, but in a limited fashion. He has not used the full projection operator, but he has used the entirely reasonable premise that (a) the dominant contamination will arise from the next highest spin state (this was suggested by Rossky and Karplus¹²), and (b) the spin contamination in the zeroth-order function will be much greater than in higher order functions, as far as energy effects are concerned. He has used these ideas successfully in a study of bond dissociation for LiH and CH₄.

In this paper we present a scheme for determining a new UMP energy series, using spin projection on the previously determined UMP wave function series, which was determined without spin projection. In other words it is still based on the simple representation for \hat{H}_0 . We shall see that there is much to be gained by spin projection, if it is done properly. We shall also present a practical spin-projected second-order scheme which, in cases where spin contamination is significant, is both more accurate and less expensive than regular unprojected UMP-4 calculations.

Method

Elementary Rayleigh-Schrödinger perturbation theory can be used to develop the standard Møller-Plesset series for the energy

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and wave function, starting from the single UHF determinant as zeroth-order wave function ψ_0 , and the usual zeroth-order Fock Hamiltonian \hat{H}_0 . The k th-order correction to the energy is

$$E_k = \langle \psi_0 | \hat{H}_1 | \psi_{k-1} \rangle \quad (1)$$

where $\hat{H}_1 = \hat{H} - \hat{H}_0$ is the first-order Hamiltonian, and ψ_k is the k th-order correction to the wave function

$$\psi_k = -(\hat{H}_0 - E_0)^{-1} (\hat{H}_1 \psi_{k-1} - \sum_{r=1}^{k-1} E_r \psi_{k-r}) \quad (2)$$

In the investigative calculations reported in this paper, these quantities are computed in the complete basis of Slater determinants; technical details may be found in ref 3 and 4.

We are concerned with developing alternative series for the correlation energy by incorporating some form of spin projection to remove the spin contamination which is present in the individual ψ_k (although it is not present in the exact wave function, in the absence of degeneracy). For this, we will use the Löwdin spin projection operator⁹

$$\hat{O} = \prod_{J \neq S} \frac{\hat{S}^2 - J(J+1)}{S(S+1) - J(J+1)} \quad (3)$$

The effect of this operator when acting on a wave function is to remove all components except that with total spin S . In a basis of Slater determinants, the action on any wave function of \hat{S}^2 (and hence \hat{O}) can be computed straightforwardly. In second quantized form, the spin operator is

$$\hat{S}^2 = \hat{S}_z^2 + \hat{S}_z + N_\beta - \sum_{ij,kl} \hat{E}_{ij}^\alpha \hat{E}_{kl}^\beta \Delta_{ij} \Delta_{kl} \quad (4)$$

where N_β is the number of occupied β spin orbitals in all determinants, \hat{E}_{ij}^α , \hat{E}_{kl}^β are spin orbital annihilation-creation operators, and Δ is the overlap matrix between the spatial parts of the α and β sets of orbitals. This operator is similar to the Hamiltonian in structure (the two electron integrals $(ij|kl)$ are replaced by $\Delta_{ij} \Delta_{kl}$), and its action on a wave function represented in a basis of determinants can be computed by using the techniques described in ref 4, with some simplifications.

It is not in general possible to simply replace ψ_0 by $\hat{O}\psi_0$ and then apply eq 1 and 2, since those equations are dependent on the zeroth-order wave function being an eigenfunction of \hat{H}_0 . Thus our approach is to use the regular Møller-Plesset theory to obtain the ψ_k 's, and then subsequently apply spin projection to obtain a series for the energy.

The complete Hamiltonian \hat{H} is spin free, and so it commutes with the operator \hat{O} . The same, however, is not true for \hat{H}_0 or \hat{H}_1 individually, since \hat{H}_0 is built from the occupied orbitals in ψ_0 , which are different for α and β spins. The exact wave function is known to satisfy the Schrödinger equation

$$\hat{H}\psi = E\psi \quad (5)$$

and so, since $[\hat{O}, \hat{H}] = 0$, it also satisfies

$$\hat{H}\hat{O}\psi = E\hat{O}\psi \quad (6)$$

Our approach is to project (6) onto some suitable trial function, and then collect terms of the same order in \hat{H}_1 to obtain a series for the energy. The first obvious choice in this context for a trial function is $\hat{O}\psi_0$, the spin projected UHF function. The k th-order energies \bar{E}_k are given by the projection of (6)

$$\langle \psi_0 | \hat{O}(\hat{H}_1 + \hat{H}_0) \hat{O} \sum_{k=0}^{\infty} |\psi_k\rangle = \sum_{r=0}^{\infty} \bar{E}_r \langle \psi_0 | \hat{O} \sum_{s=0}^{\infty} |\psi_s\rangle \quad (7)$$

(where the idempotency relation $\hat{O}^2 = \hat{O}$ has been used). This gives the series

$$\bar{E}_k = \langle \psi_0 | \hat{O} | \psi_0 \rangle^{-1} (\langle \psi_0 | \hat{O} \hat{H}_1 | \psi_{k-1} \rangle - \langle \psi_0 | \hat{O} \hat{H}_0 | \psi_{k-1} \rangle + \langle \psi_0 | \hat{O} \hat{H}_0 | \psi_k \rangle - \sum_{r=0}^{k-1} \bar{E}_r \langle \psi_0 | \hat{O} | \psi_{k-r} \rangle) \quad (8)$$

Note that straightforward application of this formula requires the evaluation of $\hat{O}\psi_0$ and $\hat{O}\hat{H}_0\hat{O}\psi_0$. In addition, \bar{E}_k contains a nonzero

contribution from ψ_k which enters through a term $\langle \psi_0 | \hat{O}(\hat{H}_0 - \bar{E}_0) \hat{O} | \psi_k \rangle$. The magnitude of this term will be expected to vary directly with the degree of spin contamination in \hat{H}_0 , since in the limit of no contamination, \hat{H}_0 commutes with \hat{O} and the term vanishes. However, we note that this presence of ψ_k does not in fact introduce extra computational difficulties; in Møller-Plesset calculations, the zeroth-order Hamiltonian is very simple, and the solution for the wave function at any order is not a problem. It is interesting to see that the energy correct to first order

$$\bar{E}_0 + \bar{E}_1 = \langle \psi_0 | \hat{O} | \psi_0 \rangle^{-1} (\langle \psi_0 | \hat{O} \hat{H}_1 | \psi_0 \rangle + \langle \psi_0 | \hat{O}(\hat{H}_0 - \bar{E}_0) \hat{O} | \psi_1 \rangle) \quad (9)$$

is not a simple expectation value, because of the presence of this term in ψ_1 ; also $\bar{E}_0 \neq E_0$.

A slightly simpler series can be generated by projecting (6) with ψ_0 alone, rather than $\hat{O}\psi_0$, i.e.

$$\langle \psi_0 | (\hat{H}_1 + \hat{H}_0) \hat{O} \sum_{k=0}^{\infty} |\psi_k\rangle = \sum_{r=0}^{\infty} \bar{E}_r \langle \psi_0 | \hat{O} \sum_{s=0}^{\infty} |\psi_s\rangle \quad (10)$$

giving

$$\bar{E}_k = \langle \psi_0 | \hat{O} | \psi_0 \rangle^{-1} (\langle \psi_0 | \hat{O} \hat{H}_1 | \psi_{k-1} \rangle - E_0 \langle \psi_0 | \hat{O} | \psi_{k-1} \rangle - \sum_{r=1}^{k-1} \bar{E}_r \langle \psi_0 | \hat{O} | \psi_{k-r} \rangle) \quad (11)$$

Here there is not contribution from ψ_k to \bar{E}_k , and it is easy to verify that $\bar{E}_0 = E_0$ and

$$\bar{E}_0 + \bar{E}_1 = \langle \psi_0 | \hat{O} | \psi_0 \rangle^{-1} \langle \psi_0 | \hat{O} \hat{H}_1 | \psi_0 \rangle \quad (12)$$

which is simply the expectation value of the Hamiltonian for the function $\hat{O}\psi_0$; thus in this case, the energy at first order is identical with that obtained in the projected UHF (PUHF) approach.

Application

In order to test the efficacy of any spin projection scheme, it is important to choose a case where any effects of spin contamination are not masked by other deficiencies of either the UHF or RHF reference functions, for example, as a molecule is stretched to dissociation. For this reason we chose to study the water molecule close to the point where the UHF and RHF wave functions first begin to differ, as the two OH bonds are stretched symmetrically. In the basis set which we used, this transition point is at approximately $1.33R_e$; here comparison of any UHF-based perturbation series with that based on RHF is meaningful since the latter is still reasonably rapidly convergent at this geometry.

All calculations were carried out in the 6-21G basis set,¹³ with the 8 valence electrons being correlated, the $1a_1$ core orbital being taken from the RHF or UHF calculation as appropriate. Calculations were carried out at a bond angle of 107.649° at a number of O-H bond distances R between $1.3R_e$ and $1.4R_e$, and also at $R = 1.5R_e$ and $R = 2R_e$ (where $R_e = 0.96658 \text{ \AA}$). Tables I-IV show the computed energies at a selection of these geometries at successive orders of perturbation theory for the Møller-Plesset series based on RHF and UHF, and the two spin-projected series presented in the preceding section.

The results indicate that up to $R \approx 1.333R_e$, RHF and UHF are identical, but beyond that point the convergence of the UHF-based series becomes considerably worse than that based on RHF orbitals; for example, at $1.35R_e$ the RHF series is converging monotonically, without any of the oscillations encountered at longer bond lengths,³ and at 4th order has already converged to within 4 mhartree of the exact energy. In contrast the UHF series is much more slowly convergent, being in error by 11 mhartree at 4th order and 3 mhartree at 8th order. This behavior is illustrated in Figures 1-4, which display the as a function of R the energies at 1st, 2nd, 4th, and 8th order of perturbation theory. At first order, which for both RHF and UHF are just the SCF energies, the UHF and RHF energies are extremely close

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TABLE I: Convergence of RMP Series for H₂O^a

	R^b				
	1.33	1.34	1.35	1.50	2.00
0 ^c	-59.401 79	-59.429 75	-59.457 37	-59.833 62	-60.701 58
1	-75.786 82	-75.782 26	-75.777 67	-75.707 21	-75.491 41
2	-75.934 99	-75.931 44	-75.927 87	-75.874 10	-75.733 05
3	-75.937 60	-75.934 02	-75.930 43	-75.876 12	-75.726 93
4	-75.948 94	-75.945 64	-75.942 33	-75.893 04	-75.773 39
5	-75.949 87	-75.946 59	-75.943 31	-75.894 39	-75.777 61
6	-75.951 72	-75.948 52	-75.945 31	-75.897 81	-75.789 98
7	-75.951 96	-75.948 76	-75.945 56	-75.898 15	-75.791 01
8	-75.952 32	-75.949 14	-75.945 96	-75.898 98	-75.795 08
var ^d	-75.952 47	-75.949 30	-75.946 12	-75.899 20	-75.791 27

^a For details of the calculation, see text. The table shows the total energies $\sum E_k$ given by successive orders of RMP perturbation theory. ^b Bond length in units of $R_c = 0.96658 \text{ \AA}$. ^c Order of perturbation theory. ^d Exact variational energy.

TABLE II: Convergence of UMP Series for H₂O^a

	R^b				
	1.33	1.34	1.35	1.50	2.00
0 ^c	-59.401 79	-59.446 23	-59.505 82	-60.204 90	-61.488 56
1	-75.786 82	-75.782 29	-75.777 99	-75.735 01	-75.699 30
2	-75.934 99	-75.928 47	-75.919 33	-75.829 39	-75.754 67
3	-75.937 60	-75.931 50	-75.923 11	-75.836 82	-75.760 22
4	-75.948 94	-75.943 33	-75.935 53	-75.848 21	-75.762 42
5	-75.949 87	-75.944 75	-75.937 82	-75.853 90	-75.763 37
6	-75.951 72	-75.947 11	-75.941 04	-75.860 35	-75.764 22
7	-75.951 96	-75.947 71	-75.942 32	-75.865 18	-75.764 88
8	-75.952 32	-75.948 39	-75.943 58	-75.869 87	-75.765 51
var ^d	-75.952 47	-75.949 30	-75.946 11	-75.899 18	-75.791 18

^a For details of the calculation, see text. The table shows the total energies $\sum E_k$ given by successive orders of UMP perturbation theory. ^b Bond length in units of $R_c = 0.96658 \text{ \AA}$. ^c Order of perturbation theory. ^d Exact variational energy.

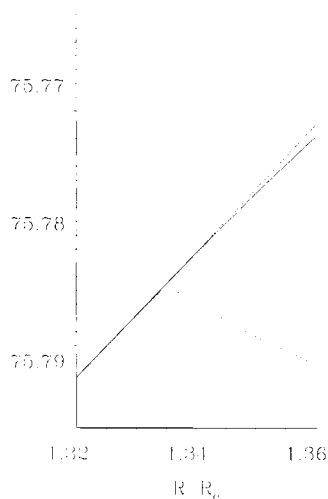


Figure 1. Comparison of first-order perturbation theory energies for symmetric stretching of H₂O: RMP (---); unprojected UMP (—); projected UMP, eq 8 (···); projected UMP, eq 11 (-·-).

in the range of geometries shown. Furthermore, the energy and its gradient are continuous at the transition point. However, at second order, the UHF energy rises considerably above that obtained from RHF orbitals, and the UHF-based energy is discontinuous in its gradient at the transition point. This discontinuity arises, of course, because the zeroth-order UHF wave function is discontinuous in its first derivative at this point, whereas the UHF energy and its gradient are continuous. The figures show very graphically the slow convergence of the UHF series beyond the transition point, and we conclude that in this region ψ_0^{UHF} , which has a very slightly lower energy than ψ_0^{RHF} but a considerably different form, is not at all a good reference function for the perturbative treatment of electron correlation effects.

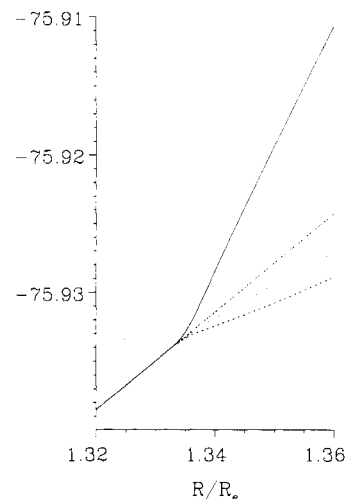


Figure 2. Comparison of second-order perturbation theory energies for symmetric stretching of H₂O. Key as in Figure 1.

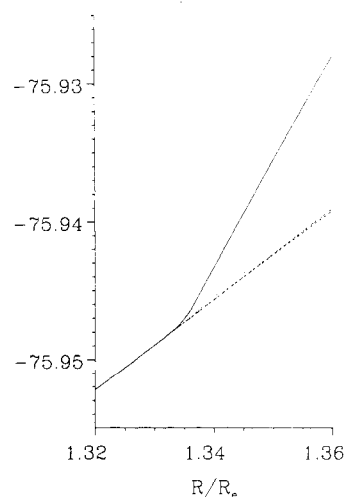


Figure 3. Comparison of fourth-order perturbation theory energies for symmetric stretching of H₂O. Key as in Figure 1.

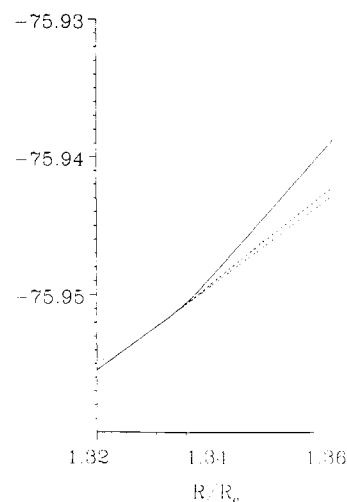


Figure 4. Comparison of eighth-order perturbation theory energies for symmetric stretching of H₂O. Key as in Figure 1.

At first order of perturbation theory, the two spin projection schemes give energies which are lower than either their UHF or RHF counterparts. However these energies are also discontinuous in their first derivative at the transition point. In particular, the second, simpler scheme of eq 11 gives rise to a spurious minimum in the potential curve; such behavior has long been known to be a serious defect of the PUHF method, to which this first-order energy is equivalent. Our first and more complicated spin pro-

TABLE III: Convergence of Projected UMP Series for H₂O^a

	<i>R</i> ^b				
	1.33	1.34	1.35	1.50	2.00
0 ^c	-59.401 79	-59.430 90	-59.459 39	-59.716 75	-60.197 72
1	-75.786 82	-75.784 12	-75.783 36	-75.772 33	-75.719 61
2	-75.934 99	-75.931 89	-75.929 41	-75.897 73	-75.787 17
3	-75.937 60	-75.934 06	-75.930 72	-75.890 99	-75.787 32
4	-75.948 94	-75.945 47	-75.941 96	-75.899 47	-75.789 57
5	-75.949 87	-75.946 32	-75.942 60	-75.897 36	-75.789 14
6	-75.951 72	-75.948 28	-75.944 64	-75.899 07	-75.789 66
7	-75.951 96	-75.948 54	-75.944 94	-75.898 53	-75.789 74
8	-75.952 32	-75.948 97	-75.945 46	-75.899 00	-75.790 09
var ^d	-75.952 47	-75.949 30	-75.946 11	-75.899 18	-75.791 18
$\langle \psi_0 \hat{S}^2 \psi_0 \rangle^e$	0.000 00	0.040 68	0.119 52	0.917 02	1.790 52
$\langle \psi_0 \hat{O}_1 \hat{S}^2 \hat{O}_1 \psi_0 \rangle$	0.000 00	0.001 48	0.013 41	1.088 60	3.544 77
$\langle \psi_0 \hat{O}_2 \hat{S}^2 \hat{O}_2 \psi_0 \rangle$	0.000 00	0.000 00	0.000 01	0.002 53	0.029 03
$\langle \psi_0 \hat{O}_3 \hat{S}^2 \hat{O}_3 \psi_0 \rangle$	0.000 00	0.000 00	0.000 00	0.000 01	0.000 04

^a For details of the calculation, see text. The table shows the total energies $\sum \bar{E}_k$ given by successive orders of projected UMP perturbation theory as defined by eq 8. ^b Bond length in units of $R_e = 0.966 58 \text{ \AA}$. ^c Order of perturbation theory. ^d Exact variational energy. ^e Expectation values of \hat{S}^2 with respect to ψ_0 . Subsequent rows show expectation values of \hat{S}^2 with respect to ψ_0 partially spin projected according to (13).

TABLE IV: Convergence of Projected UMP Series for H₂O^a

	<i>R</i> ^b				
	1.33	1.34	1.35	1.50	2.00
0 ^c	-59.401 79	-59.446 23	-59.505 82	-60.204 90	-61.488 56
1	-75.786 82	-75.785 90	-75.788 33	-75.788 65	-75.720 66
2	-75.934 99	-75.932 46	-75.930 78	-75.888 93	-75.777 97
3	-75.937 60	-75.934 45	-75.931 71	-75.887 93	-75.783 04
4	-75.948 94	-75.945 65	-75.942 40	-75.895 48	-75.785 51
5	-75.949 87	-75.946 43	-75.942 90	-75.895 57	-75.786 36
6	-75.951 72	-75.948 33	-75.944 82	-75.897 76	-75.787 22
7	-75.951 96	-75.948 58	-75.945 07	-75.898 20	-75.787 79
8	-75.952 32	-75.948 99	-75.945 55	-75.899 08	-75.788 34
var ^d	-75.952 47	-75.949 30	-75.946 11	-75.899 18	-75.791 18

^a For details of the calculation, see text. The table shows the total energies $\sum \bar{E}_k$ given by successive orders of projected UMP perturbation theory as defined by eq 11. ^b Bond length in units of $R_e = 0.966 58 \text{ \AA}$. ^c Order of perturbation theory. ^d Exact variational energy.

jection scheme of eq 8 gives no spurious minimum, but the potential curve still has a small discontinuity in its slope.

However, we are more interested in the performance of these methods in accounting for electron correlation than their behavior at first order. At second order, Figure 2, the potential energy curves are much smoother, particularly that derived from eq 8, and the very poor behavior of the unprojected second-order Møller–Plesset energy is not observed. At fourth order, Figure 3, both schemes, especially that of eq 8, give energies which are virtually identical with those obtained by using RHF orbitals, and so the perturbation series as a whole are rapidly convergent, like the RHF series. This improvement in the energies is remarkable. There is a large discontinuity in ψ_0^{UHF} as reflected by the discontinuity in the UMP-2 energies, but its effect on the perturbation series for the energy can be almost entirely smoothed out by suitable spin projection.

Furthermore, we observe that at the longer bond lengths $1.5R_e$ and $2R_e$, where the RHF-based series is not reliable except at very high order³ and one is forced to adopt a UHF reference, the spin-projected series seem to converge remarkably well, at a rate which makes them useful at low orders of perturbation theory.

We have two expressions for the new series, eq 8 and 11, with the former being more satisfactory. Both require evaluation of expectation values involving \hat{O}_l , which, according to (4), generates functions which are very highly excited with respect to ψ_0 . This presents severe computational difficulties. However, practical simplification follows by replacing \hat{O} by \hat{O}_l where

$$\hat{O}_l = \prod_{J=S+1}^{S+l} \frac{\hat{S}^2 - J(J+1)}{S(S+1) - J(J+1)} \quad (13)$$

where l is the number of bonds being broken in the distortion of the molecule under consideration ($l = 2$ for the H₂O distortions considered). Furthermore because, from (4), \hat{S}^2 is equivalent to a double excitation operator, $\hat{O}_l \psi_0$ is represented as $2l$ -fold excitation of ψ_0 . We find for H₂O that, using $l = 2$ (instead of $l = 5$), identical results to four decimal figures are found for all numbers presented in the tables. Although the use of (8) is preferable to that of (11), in practical calculations it will be more difficult. The term $\langle \psi_0 | \hat{O}_l \hat{H}_0 \hat{O}_l | \psi_k \rangle$ can be formulated as the expectation value with respect to ψ_0 of an operator containing up to $4l + 2k$ excitations; in contrast, in (11) there are no terms where \hat{O} appears more than once, and so one need only deal with $2l + 2k$ -fold excitation operators to obtain \bar{E}_k ; this in turn means that in the evaluation of the matrix elements required in (11), one need generate functions which are only $l + k$ -fold excited with respect to the reference function ψ_0 .

Therefore we recommend that, for example for a case such as H₂O where eq 13 should be used with $l = 2$, instead of calculating E_0, E_1, E_2, E_3, E_4 using eq 1, eq 11 is used to calculate \bar{E}_0, \bar{E}_1 , and \bar{E}_2 . The results to second order in Table IV are a great improvement (typically 75%) over the fourth-order results in Table II. In particular, the difference in energy between $1.33R_e$ and $2R_e$ is in error, compared to the full CI result, by just 4 mhartree when the projected second-order scheme is used, whereas UMP-4 overestimates this energy difference by 25 mhartree. The cost of calculating \bar{E}_2 is not great; it involves only the same two electron integrals which are used in E_2 , multiplied by overlap integrals between the spatial parts of the α and β orbitals. Obviously, for systems where essentially only one bond is being broken as one moves across the potential energy surface, a single spin projection term ($l = 1$ in (13)), as advocated by Schlegel,⁸ would suffice, and one could then calculate \bar{E}_3 with about the same effort as E_4 .

Finally we may summarize our results. We find that by suitable projection of the equations, after the determination of the MP wave functions, much improved series for the MP energies can be obtained. The formulas for these new energies are more complicated than the usual formulas, but the improvement is so marked that calculations at second order using the new formulas are a great improvement over the original fourth-order energies, in the cases where the latter are affected by spin contamination; we have shown that it will be practical to calculate these projected second-order energies. Our results confirm the suspicions that it is spin contamination which causes the poor convergence of the UMP series, but we express some surprise that, after projection, such good results may be obtained.

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