DECEPTIVE CONVERGENCE IN MØLLER-PLESSET PERTURBATION ENERGIES

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Møller–Plesset perturbation calculations (MPn) up to fiftieth order, within both the restricted (RHF) and unrestricted Hartree–Fock (UHF) frameworks, have been used to examine the He_2^{2+} ground-state potential curve. The bond lengths of the equilibrium and transition structures have been optimized at all orders of perturbation theory. It is found that RMPn describes the homolytic dissociation better than UMPn for all $n > 2$. This unexpected behaviour may be attributed to spin contamination in the UHF wavefunction. The UMPn barriers deceptively appear convergent for small n and the results may be indicative of dangers inherent generally in using the UMP approach with significantly spin-contaminated wavefunctions.

1. Introduction

One of the major contemporary procedures for incorporating electron correlation into molecular-orbital calculations is the use of Møller–Plesset (MP) perturbation theory [1,2]. Because the MP expansion is truncated at some finite order, use of this procedure is predicated on a rapid convergence of the MP series.

Efficient methods have been devised for calculating the Møller–Plesset energy to second (MP2), third (MP3) or fourth (MP4) order [2,3] and it is of interest to enquire how close the MP4 results are to the limiting values. This has been done in a small number of cases by comparison with results of full configuration interaction (CI) calculations (see, for example, refs. [4,5]), but the latter are available for only a very limited number of molecules.

An alternative, less rigorous means of assessing convergence involves examining the changes that occur in progressing from Hartree–Fock (HF) (which is equivalent to MP1) to MP2 to MP3 to MP4. If these changes decrease in magnitude smoothly towards small values, this might be taken as an indication of a close approach to the limiting value.

One situation where the full CI result is readily accessible is for two-electron systems since, in these cases, full CI is achieved through straightforward

CISD (CI with all single and double excitations) calculations. The MP2, MP3 and MP4 results may also be obtained routinely and compared with the full CI result. We have found, in this manner, an example of deceptive convergence of the Møller–Plesset energies for one such two-electron system, namely the recently observed [6] dihelium dication (He_2^{2+}). Results relevant to this point are presented here.

In addition, recursion formulae have been derived which allow the evaluation of Møller–Plesset energies to any finite order for minimal-basis-set calculations on the He_2^{2+} system. This enables a critical examination of the convergence behaviour of restricted (RMP) and unrestricted Møller–Plesset (UMP) calculations.

2. Method and results

Using a modified version [7] of the GAUSSIAN 82 system of programs [8], standard ab initio calculations were carried out for He_2^{2+}, both for the equilibrium structure and for the transition structure linking the molecule to two He^+ ions.

In an initial set of calculations, the equilibrium bond length in He_2^{2+} was optimized at each of twenty different levels of theory. These arise from combining successively each of four different basis sets with each of five different methods of incorporating elec-

tron correlation. The basis sets used were:

(1) a minimal basis [‡] containing a single s function on each helium atom $(3s) \rightarrow [1s]$;

(2) a double-zeta basis, 3-21G [9], with two s functions on each helium atom: $(3s) \rightarrow [2s]$;

(3) a double-zeta plus polarisation basis, 6-31G** [10] with two s and a set of p functions on each helium atom: $(4s1p) \rightarrow [2s1p]$;

(4) a "large" basis consisting of the 6-311G set which includes three s functions [11] supplemented by three sets of p and a set of d functions [12] on each of the helium atoms: $(5s3p1d) \rightarrow [3s3p1d]$.

These were used in conjunction with restricted Hartree–Fock theory (RHF), Møller–Plesset perturbation theory terminated at second, third and fourth order (RMP2, RMP3 and RMP4), and full configuration interaction (CI).

In a second set of calculations, the bond length of the transition structure which leads to the dissociation of the dication into two monocations was obtained. The He_2^{2+} system is RHF→UHF unstable when the He–He distance exceeds about 0.85 Å and since the transition structure has a bond length significantly greater than this, we can use either the restricted or unrestricted Hartree–Fock molecular

‡ Formed by contraction of the 3-21G basis set, the coefficients being derived from a 3-21G calculation on He_2^{2+} at a bond length of 0.7 Å.

orbitals (RHF and UHF, respectively) as the starting point for the Møller–Plesset perturbation calculations. We have explored both possibilities and, in so-doing, have calculated the bond length and energy of the transition structure at 36 different levels. These arise from all possible combinations of each of our four basis sets with each of RHF, RMP2, RMP3, RMP4, UHF, UMP2, UMP3, UMP4 and CI. The computed barriers at each of these levels of theory are summarized in tables 1 and 2.

The potential curve for He_2^{2+} has been accurately calculated via the James–Coolidge method by Yagisawa et al. [13]. Their results indicate that the curve possesses a local minimum at $r = 0.70$ Å and a local maximum (the transition structure) at $r = 1.15$ Å and that the energy difference between the two extrema is 145 kJ mol^{-1}. We use these values as the standards by which to judge the predictions of each of the levels of theory which we have used.

Finally, we derived recursion formulae which enable us to calculate fifth-order and higher terms in the Møller–Plesset energy expansion for He_2^{2+} with an arbitrary minimal basis set. In this way, we have calculated (for our smallest basis set) RMPn and UMPn potential curves for He_2^{2+} $(0.55 \le r \le 1.45$ Å) for n ranging from 2 to 50, and have constructed an optimizer to locate the local minimum and maximum on each of these curves. Some of the results of these calculations are summarized in table 3 and fig. 1.

Table 1
Calculated barrier heights using RHF orbitals (kJ mol^{-1})

Basis set		RHF	RMP2	RMP3	RMP4	Full CI
(3s)	→[1s]	924	313	145	96	102
(3s)	→[2s]	610	191	82	46	33
(4s1p)	→[2s1p]	794	337	199	147	130
(5s3p1d)	→[3s3p1d]	805	345	210	157	139

Table 2
Calculated barrier heights using UHF orbitals (kJ mol^{-1})

Basis set		UHF	UMP2	UMP3	UMP4	Full CI
(3s)	→[1s]	161	228	250	252	102
(3s)	→[2s]	108	160	175	173	33
(4s1p)	→[2s1p]	164	237	256	257	130
(5s3p1d)	→[3s3p1d]	166	251	266	266	139

Table 3
Optimized bond lengths (Å) and barrier heights (kJ mol^{-1}) at minimal-basis-set RMPn and UMPn levels

| n	r_e	RMP		UMP	
		r_{TS}	barrier	r_{TS}	barrier
1	0.6759	2.1434	924.1	0.9211	161.0
2	0.6985	1.2497	312.5	0.9671	228.3
3	0.7140	1.0809	145.1	0.9874	250.4
4	0.7219	1.0284	96.3	1.0021	251.8
5	0.7248	1.0211	85.5	1.0143	245.7
6	0.7255	1.0362	88.4	1.0248	237.6
7	0.7254	1.0643	95.9	1.0342	229.6
8	0.7253	1.0957	102.9	1.0426	222.3
9	0.7252	1.1015	105.7	1.0505	215.5
10	0.7252	1.0884	105.0	1.0579	209.3
11	0.7251	1.0775	103.5	1.0648	203.7
12	0.7251	1.0716	102.4	1.0715	198.4
13	0.7251	1.0699	101.9	1.0778	193.6
14	0.7251	1.0707	101.8	1.0838	189.1
15	0.7251	1.0727	102.0	1.0895	184.9
16	0.7251	1.0745	102.2	1.0950	181.0
17	0.7251	1.0752	102.3	1.1002	177.3
18	0.7251	1.0750	102.4	1.1052	173.9
19	0.7251	1.0744	102.3	1.1099	170.6
20	0.7251	1.0740	102.3	1.1146	167.5
∞	0.7251	1.0740	102.3	1.0740	102.3
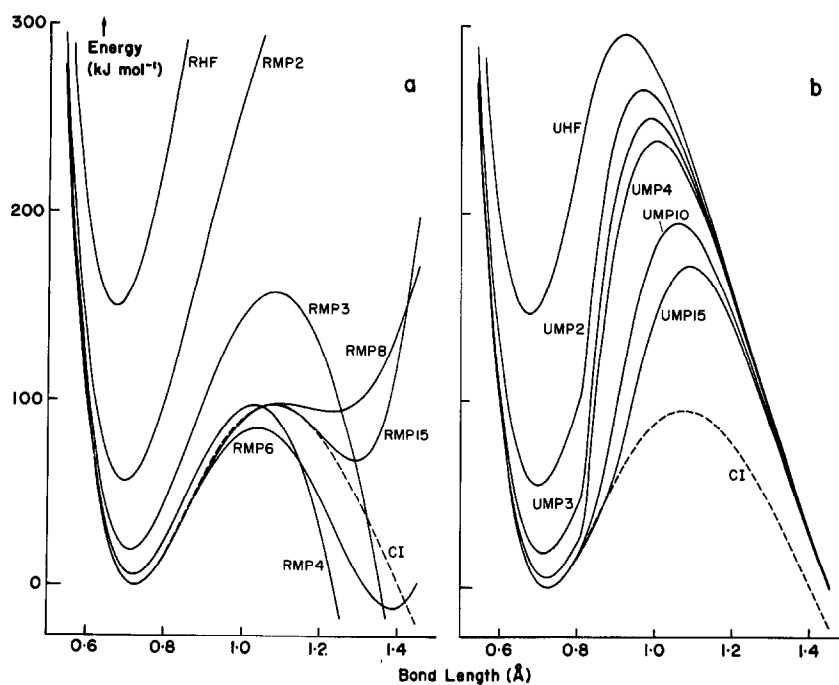
Fig. 1. Potential curves for He$_2^+$ at (a) minimal-basis-set RMPn ($n=1, 2, 3, 4, 6$ and 8) and (b) minimal-basis-set UMPn ($n=1, 2, 3, 4, 10$ and 15) levels.

3. Discussion

Restricted Hartree–Fock theory gives a correct qualitative description of the heterolytic dissociation of He_2^{2+} into $He + He^{2+}$ but is incapable of correctly describing the lower-energy homolytic fission (to $He^+ + He^+$) in which we are interested. In contrast, the unrestricted theory provides a qualitatively correct account of the energetics of both processes. However, when the RHF and UHF wavefunctions differ, only the former is an eigenfunction of the S^2 operator. The ground state ($^1\Sigma_g^+$) of He_2^{2+} is a singlet, $\langle S^2 \rangle = 0$, for all internuclear distances through to the dissociation limit [13], but as the bond is stretched beyond 0.85 Å the UHF wavefunction becomes progressively more and more contaminated by a (higher-energy) triplet state ($^3\Sigma_u^+$) with $\langle S^2 \rangle = 2$. At infinite separation, where the RHF wavefunction is still a singlet, the UHF wavefunction has become an equal mixture of singlet and triplet states and consequently $\langle S^2 \rangle = 1$. It is important therefore to realize that while the UHF wavefunction "dissociates correctly" in an energetic sense, the wavefunction itself becomes a progressively poorer and poorer approximation as the bond length increases. That crucial distinction lies at the heart of this paper.

We see initially that full electron correlation, within a sufficiently large basis set, gives a satisfactory account of the barrier height. The values shown in tables 1 and 2 closely approach the result of Yagisawa et al. [13].

Restricted Hartree–Fock theory itself, even with our largest basis set, overestimates the barrier by more than a factor of five (table 1). However, when second-order perturbation theory based on these restricted orbitals is used, the barrier is reduced dramatically to less than half of the RHF value. Third- and fourth-order treatments continue the improvement to the point where the RMP4 estimate of the barrier height differs from the full CI value by only 13%.

Table 2 tells a very different story. The barrier is overestimated using unrestricted Hartree–Fock theory by about 20% with our best basis set and by larger proportions with the smaller sets. However, in stark contrast to the results of table 1, second- and third-order perturbation treatments based on these UHF orbitals serve only to *increase* the estimate of the bar-

rier height, and this peculiar effect occurs in a qualitatively similar fashion irrespective of which of our basis sets is used. The fourth-order correction is very small ($0-2$ kJ mol^{-1}) and it too is almost independent of the particular basis set chosen. Moreover, so small are all the fourth-order corrections in table 2, and so smooth is the variation in barrier height from UHF to UMP4 (fig. 2), that it would be very tempting indeed to interpret these as evidence that the UMP series has converged and that, for example, the barrier using our largest basis set and a full correlation treatment is close to 266 kJ mol^{-1}, when in fact it is only 139 kJ mol^{-1}!

The explanation for this deceptive convergence is clear from fig. 1b. In progressing from UMP3 to UMP4, the energies of the equilibrium and transition structures are lowered by almost exactly the same amount, so that the barrier height remains virtually unchanged. However, while almost all (96.5%) of the minimal-basis-set correlation energy at the equilibrium structure has been recovered by the fourth-order treatment, a very much smaller fraction (28.1%) has been recovered at the transition structure. The energy of the transition structure will therefore continue to drop as higher-order perturbation terms are included, leading ultimately to the substantial decrease in barrier height required to give the full CI result.

To what can we attribute these difficulties? In Møller–Plesset perturbation theory, the starting point
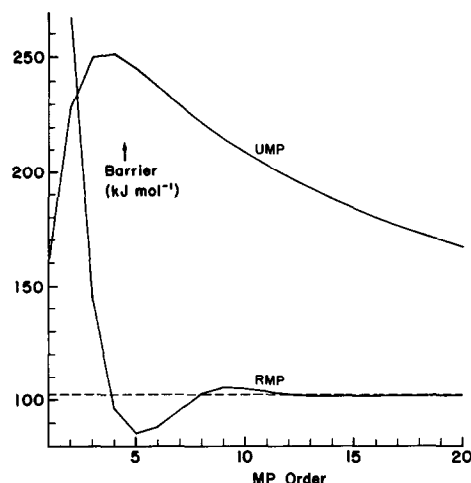

Fig. 2. Barriers to homolytic fission of He_2^{2+} using minimal-basis-set MPn theory ($n = 1-20$).

is a Hartree–Fock wavefunction, and the energy expansion will converge rapidly only if that wavefunction is sufficiently similar to the exact wavefunction. While the Hartree–Fock orbitals are a good starting point for He_2^{2+} at its equilibrium geometry, no single-determinant, restricted or unrestricted, offers a completely satisfactory zeroth-order wavefunction at the transition structure. The UMP perturbation series for the energy of the transition structure converges smoothly, but also slowly compared with that for the minimum that estimates of the barrier height drastically exaggerate it, even when many terms in the series are included. Conversely, as we shall see below, the RMP series for the transition structure, while converging much more quickly, does so in an oscillatory fashion. One consequence of this is that the sequence of RMP estimates of the barrier height also oscillates. Similar patterns of behaviour have been observed for the RMP and UMP expansions by Handy and co-workers [4] in the cases of stretched H_2O and NH_2 molecules.

These conclusions may be demonstrated quantitatively by an analytical examination of the convergence properties of both the restricted and unrestricted MP series beyond MP4. To do this requires non-standard methods since current state-of-the-art general-purpose programs such as GAUSSIAN 82 offer MP calculations only up to and including fourth-order. Although, in the general case, the calculation of higher-order energies is computationally very demanding and the programming of the specific formulae for the MPn energies is extremely complex [4,5], it turns out that, in the special case of a system with just two electrons and two basis functions, the task becomes comparatively simple. Fortunately, such a treatment is sufficient for our problem since the qualitative behaviour of MP theory with large basis sets is reproduced by our minimal set (tables 1 and 2). We have, in this way, been able to develop exact recursion formulae for the perturbation energies of He_2^{2+} with a minimal basis set. The computational effort required to evaluate the nth-order perturbation energy using such formulae increases only linearly with n compared with the exponential dependence on n in the previously used, more general procedures [4,5].

In a UHF framework, the interaction of two helium s orbitals results in two bonding spin orbitals ψ_1^α and

ψ_1^β (both with orbital energy ϵ_1) and two antibonding spin orbitals ψ_2^α and ψ_2^β (both with orbital energy ϵ_2). The full correlation energy in this model is found as the lowest eigenvalue of the matrix

$$\mathbf{H} = \begin{vmatrix} 0 & 0 & K_2 \\ 0 & \alpha_1 - x^{-1} & K_1 \\ K_2 & K_1 & 2\alpha_2 - 2x^{-1} \end{vmatrix} ,$$

which arises from expanding the CI wavefunction $|\Psi\rangle$ as a linear combination of the ground, (spin-adapted) singly excited and doubly excited configurations

$$|\Psi\rangle = |\Psi_0\rangle + c_1 |\Psi_1\rangle + c_2 |\Psi_2\rangle \qquad (1)$$

and then removing the Hartree–Fock energy. We use K_1, K_2, α_1 and α_2 to represent combinations of appropriate molecular integrals and $x = (\epsilon_1 - \epsilon_2)^{-1}$.

The eigenvalue problem reduces to a cubic equation for the correlation energy E:

$$(1 - \alpha_1 x + xE)[xE^2 + (2 - 2\alpha_2 x)E - K_2^2 x]$$
$$= K_1^2 x^2 E , \qquad (2a)$$

which, in the special case of RHF (where $K_1 = 0$ by symmetry), reduces to

$$xE^2 + (2 - 2\alpha_2 x)E - K_2^2 x = 0 . \qquad (2b)$$

The term in x^k in the Maclaurin expansion of $E(x)$ is then the $(k+1)$th-order perturbation correction to the Hartree–Fock energy, i.e.

$$E = c_1 x + c_2 x^2 + c_3 x^3 + ...$$
$$= E_2 + E_3 + E_4 + ... \qquad (3)$$

The E_i are most conveniently evaluated using recursion formulae. Defining

$$T_1 = \alpha_1 + \alpha_2 , \quad T_2 = \tfrac{1}{2}(K_1^2 + K_2^2) - \alpha_1 \alpha_2 ,$$
$$T_3 = \tfrac{1}{2}\alpha_1 + \alpha_2 ,$$
$$\gamma_n = \sum_{i=2}^{n-2} E_i E_{n-i} , \quad \delta_n = \sum_{i=2}^{n-4} E_i \gamma_{n-i} ,$$

it eventually follows that the nth-order Møller–Plesset correction to the energy is given by

$$E_n = x T_1 E_{n-1} - \tfrac{3}{2} x \gamma_n + T_2 x^2 E_{n-2} + T_3 x^2 \gamma_{n-1}$$

$$- \tfrac{1}{2} x^2 \delta_n \, , \quad n > 3 \, , \tag{3a}$$

which, in the RHF case, becomes the much simpler

$$E_n = x(\alpha_2 E_{n-1} - \tfrac{1}{2} \gamma_n) \, , \quad n > 2 \, . \tag{3b}$$

Using these formulae (once K_1, K_2, α_1, α_2 and x are known for a chosen bond length), the terms in the RMP and UMP series become almost trivial to evaluate.

The results of table 3 show that the equilibrium bond length in He_2^{2+} is a very heavily damped oscillating function of n, the order of MP theory used. The value at MP4 differs from the full CI length by only 0.003 Å and at MP5 this difference is reduced by another order of magnitude.

In contrast, the bond length in the transition structure either oscillates over a much greater range (in the RMP case), or progresses very slowly up to, beyond, and finally back to its limiting value (in the UMP case). For example, UHF gives a bond length which is 0.15 Å too short, UMP4 still underestimates the CI value by more than 0.07 Å, the UMP12 length is almost correct, and the UMP20 estimate is 0.04 Å too long!

The barrier height (table 3 and fig. 2) plunges very rapidly over the first five orders of RMP theory and then oscillates with a rapidly decreasing amplitude about the full CI value. So-called "chemical accuracy" is attained above RMP7. However, with UMP theory, as we observed earlier, the barrier actually increases over the first four orders and only beyond UMP4 does it begin its extremely slow descent to the correct value. One unfortunate consequence of this unexpected behaviour is that the worst estimate by any order of UMP theory (including UHF itself) is that given by UMP4 and, compounding the problem, the fourth-order term E_4 is sufficiently small that, given only the barriers at levels up to and including UMP4, one could easily reach the false conclusion that convergence had been achieved.

The problems associated with the UMP treatment may undoubtedly be attributed to spin contamination in the UHF wavefunction. The $\langle S^2 \rangle$ values in the vicinity of the transition structure are typically 0.5–0.8 compared with the 0.0 required for a pure singlet. Spin-projected Møller–Plesset theory, as recently introduced by Schlegel [14], may offer a

promising mechanism for overcoming the spin-contamination problem. In the case of our minimal-basis He_2^{2+} system, the full spin-projected formalism is particularly easy to apply since there is only triplet contamination, and such calculations are in progress.

4. Conclusions

Møller–Plesset perturbation theory provides a practically useful method of incorporating electron correlation only when the Hartree–Fock wavefunction upon which the theory is based is a sufficiently good zeroth-order approximation to the true wavefunction. In cases where a UHF wavefunction is significantly contaminated by states of higher multiplicities this proviso is not satisfied. In the example which we have studied, more accurate estimates of both geometries and barriers are obtained by using RMPn uniformly along the entire potential curve than by using UMPn for any n greater than 2. That this is found to be the case indicates that the "incorrect dissociation" behaviour of RHF does not impede the rapid convergence of the Møller–Plesset series as much as the presence of a triplet contaminant in the UHF wavefunction does. We believe that this is likely to be true in general and that caution should be exercised before applying UMP theory to heavily spin-contaminated wavefunctions.

References

[1] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.

[2] J.A. Pople, J.S. Binkley and R. Seeger, Intern. J. Quantum Chem. Symp. 10 (1976) 1.

[3] J.A. Pople, R. Krishnan, H.B. Schlegel and J.S. Binkley, Intern. J. Quantum Chem. 14 (1978) 545;
R. Krishnan, M.J. Frisch and J.A. Pople, J. Chem. Phys. 72 (1980) 4244.

[4] N.C. Handy, P.J. Knowles and K. Somasundram, Theoret. Chim. Acta 68 (1985) 87, and references therein.

[5] W.D. Laidig, G. Fitzgerald and R.J. Bartlett, Chem. Phys. Letters 113 (1985) 151, and references therein.

[6] M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenovic and P. von R. Schleyer, J. Phys. B17 (1984) L605.

[7] J. Baker, R.H. Nobes, D. Poppinger and M.W. Wong, unpublished;
J. Baker, J. Comput. Chem., to be published.

[8] J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder and J.A. Pople, GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, USA.

[9] J.S. Binkley, J.A. Pople and W.J. Hehre, J. Am. Chem. Soc. 102 (1980) 939.

[10] W.J. Hehre, R. Ditchfield and J.A. Pople, J. Chem. Phys. 56 (1972) 2257;
P.C. Hariharan and J.A. Pople, Theoret. Chim. Acta 28 (1973) 213.

[11] R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, J. Chem. Phys. 72 (1980) 650.

[12] M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80(1984) 3265.

[13] H. Yagisawa, H. Sato and T. Watanabe, Phys. Rev. A16 (1977) 1352.

[14] H.B. Schlegel, J. Chem. Phys. 84 (1986) 4530.