

Why does unrestricted Møller–Plesset perturbation theory converge so slowly for spin-contaminated wave functions?

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The poor convergence of the unrestricted Møller–Plesset (UMP) series for some systems and the presence of significant spin contamination in the underlying unrestricted Hartree–Fock (UHF) wave functions have both been shown to result from the presence of low-lying, doubly excited determinants. The contributions to the UCI energy from any determinants which mix with the UHF wave function through the problematic doubly excited determinants will be described poorly by UMP theory.

I. INTRODUCTION

It is common for the effects of electron correlation to be incorporated into molecular-orbital calculations through the use of Møller–Plesset (MP) perturbation theory.^{1,2} In this approach, the full-CI energy of a system is expanded as an infinite series in the Møller–Plesset λ parameter and the partial sum, if the series is truncated at n th order, is termed the MP_n energy of the system.

In general, the zeroth-order wave function on which an MP expansion is based is a spin-unrestricted Hartree–Fock (UHF) wave function and the application of Møller–Plesset theory leads to UMP_n energies. For closed-shell species near their equilibrium geometries, the UHF wave function may reduce to a restricted Hartree–Fock (RHF) wave function, leading to RMP_n energies. However, where this reduction does not occur, and in open-shell species where it cannot occur, the UHF wave function is normally contaminated by electronic states of higher spin multiplicity and is thus no longer an eigenfunction of the S^2 (spinsquared) operator (i.e., $\langle S^2 \rangle_{UHF}$ for singlets > 0.0 , $\langle S^2 \rangle_{UHF}$ for doublets > 0.75 , etc.).

In a number of recent papers,^{3–5} it has been found that spin contamination in the underlying UHF wave function appears to be associated with slow convergence of the corresponding Møller–Plesset perturbation series. Handy *et al.*³ and Gill *et al.*⁴ have observed poor UMP convergence in stretched molecules (H_2O , NH_2 , and He_2^+), in which extensive spin contamination arises from the presence of partially homolytically broken bonds, while Nobes *et al.*⁵ have studied the cyano radical (CN^\cdot) for which, even at its equilibrium geometry, the UHF wave function is heavily contaminated ($\langle S^2 \rangle = 1.23$ at the UHF/STO-3G//UHF/6-31G* level) and the UMP series converges very slowly.

In response to the problem, both Schlegel⁶ and Knowles *et al.*⁷ have developed the formalism of spin-projected Møller–Plesset perturbation (PMP) theory and Gill *et al.*⁸ have explored the circumstances under which the RMP se-

ries for a singlet system may possess superior convergence characteristics to, and should therefore be used instead of, the UMP series. Although both of these approaches can be very useful, each has its limitations. Spin-projected MP theory is not computationally tractable in its complete form and, generally, it is feasible to project out only one or two of the contaminants. As a consequence, practical implementations of the method sometimes generate peculiar artefacts (e.g., kinks⁶) on potential surfaces. On the other hand, poorly convergent UMP theory can be usefully replaced by RMP theory only for closed-shell species and only within certain regions of a given potential surface.⁸

With this background, it now seems appropriate to address the following, hitherto neglected, questions:

- (1) Why do the unrestricted MP series for certain systems converge so slowly?
- (2) What is the relationship, if any, between poor UMP convergence and the deviation in $\langle S^2 \rangle_{UHF}$ from the values appropriate to a pure spin state?

In the present paper, we have undertaken a detailed analysis of the mechanism by which full CI and MP theory incorporate electron correlation into minimal-basis-set calculations on the H_2 system. We find that the correlation behavior in a stretched H_2 molecule can be understood in terms of a simple model which can also be used to rationalize the poor UMP convergence observed for the HCC^\cdot and CN^\cdot radicals. We demonstrate that a fundamental connection exists between the rate of UMP convergence, the extent of spin contamination in the associated UHF wave function, and the importance of certain double excitations in the UHF-based CI expansion.

II. METHOD AND RESULTS

Using a graphical unitary group (GUGA) CI program⁹ and a modified version¹⁰ of the GAUSSIAN 86 system of programs,¹¹ standard *ab initio* calculations¹² were carried out on the three systems H_2 , CN^\cdot , and HCC^\cdot . The minimal STO-3G basis set and the unrestricted Hartree–Fock

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TABLE I. Total energies and percentage of electron correlation energy recovered (UHF, UMP2, UMP3, UMP4, and full CI, in hartrees), $\langle S^2 \rangle$ values, and UCI single (a_1^2) and double (a_{11}^{22}) coefficients^a for the H₂ molecule as a function of bond length (r , Å) (STO-3G basis set).

r	UHF	UMP2	UMP3	UMP4	CI	$\langle S^2 \rangle^b$	a_1^2	a_{11}^{22}	Λ^c
0.75	-1.116 15 0.0%	-1.129 52 63.8%	-1.134 48 87.4%	-1.136 25 95.9%	-1.137 12 100%	0.00	0.000	0.115	2.508
1.35	-0.975 55 0.0%	-0.983 09 15.2%	-0.988 45 26.1%	-0.992 83 34.9%	-1.025 05 100%	0.49	0.268	0.452	1.381
2.00	-0.937 21 0.0%	-0.937 32 1.0%	-0.937 42 1.8%	-0.937 51 2.6%	-0.948 64 100%	0.95	0.206	0.902	1.037
2.50	-0.933 87 0.0%	-0.933 87 0.1%	-0.933 87 0.3%	-0.933 88 0.4%	-0.936 05 100%	0.99	0.094	0.982	1.003

^a Using intermediate normalization.

^b The expectation value of the S^2 operator over the UHF wave function.

^c Radius of convergence of the UMP series for the UCID energy.

(UHF) framework were used for all of the calculations performed.

In an initial investigation, the total energy of the H₂ molecule was calculated for a number of values of the bond length ($r = 0.75, 1.35, 2.00,$ and 2.50 Å) using each of the first four orders of Møller–Plesset perturbation theory (UHF, UMP2, UMP3, and UMP4) and full CI. Subsequently, the total energies of the cyano (CN[•]) and ethynyl (HCC[•]) radicals were calculated using UHF, UMP2, UMP3, UMP4 and full CI in conjunction with a number of post-SCF windows. The results for the H₂, CN[•], and HCC[•] systems are summarized in Tables I, II, and III, respectively. The data obtained for the three species enable a detailed analysis to be made of the efficiency with which Møller–Plesset perturbation theory recovers the electron correlation energy in such systems.

III. THE HARTREE–FOCK DESCRIPTIONS OF H₂ (MINIMAL BASIS SET)

We begin by studying the minimal-basis-set description of the H₂ molecule. An RHF calculation on this system leads

to two molecular orbitals: ψ_o (occupied) and ψ_u (unoccupied). By considering all possible excitations of the two electrons, we obtain the four RHF determinants depicted in Fig. 1. Because ψ_o and ψ_u have σ_g^+ and σ_u^+ symmetry (in the $D_{\infty h}$ point group), respectively, only C (the doubly excited determinant) can mix with R (the Hartree–Fock determinant). Thus, the exact (minimal basis set, full CI) wave function for the H₂ molecule is given (using RHF intermediate normalization) by

$$\Psi_{\text{exact}} = R - \mu C, \quad (3.1)$$

where the coefficient μ depends, in general, on the bond length and basis set used. We note, however, that, at infinite separation ($r = \infty$), ψ_o and ψ_u become degenerate, R and C also become degenerate, and $\mu(r = \infty) = 1$.

Beyond a critical bond length r_{crit} , it becomes energetically favorable for the orbitals in H₂ to break symmetry (with respect to the center of inversion) and become more localized about one or other nucleus. This can only take place if the spin restriction of the RHF formalism is removed, leading thereby to the UHF determinants shown in

TABLE II. Total energies and percentage of electron correlation energy recovered (UMP2, UMP3, UMP4, and CI, in hartrees) for CN[•] radical within various correlation windows (STO-3G basis set).^a

Window	UMP2	UMP3	UMP4	UCI ^b	UCISD coefficients		
					$\pi\pi \rightarrow \pi\pi^c$	$\pi \rightarrow \pi^d \sigma \rightarrow \sigma^e$...
$\{\pi_x, 5\sigma, \pi_x^*\}$	-91.033 24	-91.037 40	-91.040 23	-91.049 12	0.214	0.100	...
	30.1%	48.4%	60.9%	100%			
$\{4\sigma, 5\sigma, \pi_x^*\}$	-91.027 77	-91.028 37	-91.028 63	-91.028 85	0.004
	56.1%	80.5%	91.1%	100%			
$\{4\sigma, \pi_x, 5\sigma, \pi_x^*\}$	-91.038 80	-91.045 13	-91.049 45	-91.065 04 ^f	0.216	0.153	0.112
	32.1%	48.5%	59.7%	100%			
Frozen core ^g	-91.102 87	-91.112 62	-91.127 14	-91.179 72	0.175	0.168	0.138
	49.9%	56.2%	65.7%	100%			

^a $r_{\text{CN}} = 1.235$ Å, UHF energy = -91.026 39, $\langle S^2 \rangle_{\text{UHF}} = 1.564$.

^b Full CI values, unless otherwise noted.

^c The doubly excited determinant $\pi_x(\alpha)\pi_x(\beta) \rightarrow \pi_x^*(\alpha)\pi_x^*(\beta)$.

^d The singly excited determinant $\pi_x(\alpha) \rightarrow \pi_x^*(\alpha)$.

^e The singly excited determinant $4\sigma(\beta) \rightarrow 5\sigma(\beta)$.

^f UCISD value.

^g Window comprises all molecular orbitals in Fig. 4 except 1σ and 2σ .

TABLE III. Total energies and percentage of electron correlation energy recovered (UMP2, UMP3, UMP4, and CI, in hartrees) for HCC radical within various correlation windows (STO-3G basis set).^a

Window	UMP2	UMP3	UMP4	UCI ^b	UCISD coefficients		
					$\pi\pi \rightarrow \pi\pi^c$	$\pi \rightarrow \pi^d$	$\sigma \rightarrow \sigma^e$
$\{\pi_x, 5\sigma, \pi_x^*\}$	-75.204 14	-75.208 62	-75.211 38	-75.218 07	0.191	0.086	...
	36.6%	57.0%	69.5%	100%			
$\{4\sigma, 5\sigma, \pi_x^*\}$	-75.196 53	-75.196 67	-75.196 72	-75.196 76	0.002
	64.6%	86.2%	93.8%	100%			
$\{4\sigma, \pi_x, 5\sigma, \pi_x^*\}$	-75.205 76	-75.210 69	-75.213 68	-75.220 97 ^f	0.190	0.093	0.025
	38.8%	58.6%	70.7%	100%			
Frozen core ^g	-75.279 34	-75.292 63	-75.304 27	-75.336 61	0.155	0.123	0.022
	59.2%	68.7%	77.0%	100%			

^a $r_{\text{HC}} = 1.067 \text{ \AA}$, $r_{\text{CC}} = 1.221 \text{ \AA}$, UHF energy = -75.196 11, $\langle S^2 \rangle_{\text{UHF}} = 1.358$.

^b Full CI values, unless otherwise noted.

^c The doubly excited determinant $\pi_x(\alpha)\pi_x(\beta) \rightarrow \pi_x^*(\alpha)\pi_x^*(\beta)$.

^d The singly excited determinant $\pi_x(\alpha) \rightarrow \pi_x^*(\alpha)$.

^e The singly excited determinant $4\sigma(\beta) \rightarrow 5\sigma(\beta)$.

^f UCISD value.

^g Window comprises all molecular orbitals in Fig. 4 (including the 7σ MO) except 1σ and 2σ .

Fig. 2. All four UHF orbitals ($\psi_o^\alpha, \psi_o^\beta, \psi_u^\alpha, \psi_u^\beta$) possess σ^+ symmetry (in the $C_{\infty v}$ point group) and, consequently, all four determinants can mix in the unrestricted CI wave function.

Following Szabo and Ostlund,¹³ we express the UHF orbitals in terms of the RHF orbitals through the following unitary transformations:

$$\begin{bmatrix} \psi_o^\alpha \\ \psi_u^\alpha \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \psi_o \\ \psi_u \end{bmatrix}, \quad (3.2a)$$

$$\begin{bmatrix} \psi_o^\beta \\ \psi_u^\beta \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \psi_o \\ \psi_u \end{bmatrix}, \quad (3.2b)$$

where the “symmetry breaking” parameter θ ranges in value from $\theta = 0$ (corresponding to completely delocalized orbitals, i.e., $r < r_{\text{crit}}$. UHF orbitals the same as RHF orbitals) to $\theta = \pi/4$ (corresponding to completely localized orbitals, i.e., $r = \infty$). Similarly, using the relationships in Eq. (3.2), we can express the UHF determinants (U, A', B' , and C' , Fig. 2) in terms of the RHF determinants (R, A, B , and C , Fig. 1) as follows:

$$\begin{bmatrix} U \\ A' \\ B' \\ C' \end{bmatrix} = \begin{bmatrix} \cos^2 \theta & \sin \theta \cos \theta & -\sin \theta \cos \theta & -\sin^2 \theta \\ -\sin \theta \cos \theta & \cos^2 \theta & \sin^2 \theta & -\sin \theta \cos \theta \\ \sin \theta \cos \theta & \sin^2 \theta & \cos^2 \theta & \sin \theta \cos \theta \\ -\sin^2 \theta & \sin \theta \cos \theta & -\sin \theta \cos \theta & \cos^2 \theta \end{bmatrix} \begin{bmatrix} R \\ A \\ B \\ C \end{bmatrix}. \quad (3.3)$$

We note that, when $\theta = 0$, the UHF determinants U, A', B' , and C' reduce exactly to the RHF determinants R, A, B , and C , respectively.

Because the normalized (spin-adapted) RHF configuration state functions R, C , and $(A - B)/\sqrt{2}$ can all be shown to be pure spin states:

$$S^2[R] = 0 \cdot [R] \quad \text{i.e., } R \text{ is a singlet,} \quad (3.4a)$$

$$S^2[C] = 0 \cdot [C] \quad \text{i.e., } C \text{ is a singlet,} \quad (3.4b)$$

$$S^2[(A - B)/\sqrt{2}] = 2 \cdot [(A - B)/\sqrt{2}] \quad \text{i.e., } [(A - B)/\sqrt{2}] \text{ is a triplet,} \quad (3.4c)$$

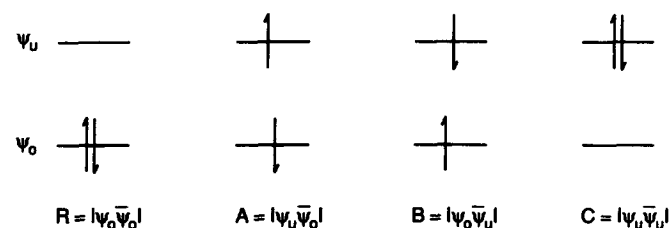


FIG. 1. The four possible RHF determinants for H₂, using a minimal basis set.

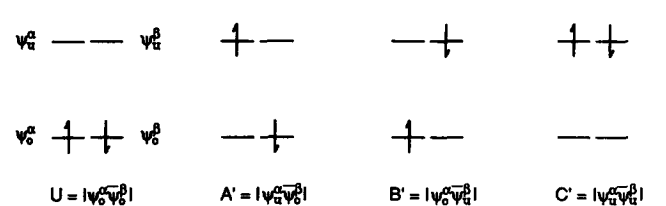


FIG. 2. The four possible UHF determinants for H₂, using a minimal basis set.

it is now straightforward to use Eqs. (3.3) and (3.4) to relate $\langle S^2 \rangle_{\text{UHF}}$ to the θ parameter. From Eq. (3.3), the UHF wave function

$$U = R \cos^2 \theta + (A - B) \sin \theta \cos \theta - C \sin^2 \theta \quad (3.5)$$

and, using Eq. (3.4), it follows that

$$\begin{aligned} \langle S^2 \rangle_{\text{UHF}} &= \langle U^* | S^2 | U \rangle \\ &= 2 \langle (A - B) / \sqrt{2} | S^2 | (A - B) / \sqrt{2} \rangle \\ &\quad \times \sin^2 \theta \cos^2 \theta \\ &= (2)(2) \sin^2 \theta \cos^2 \theta = \sin^2 2\theta. \end{aligned} \quad (3.6)$$

This remarkably simple expression shows that, near the equilibrium bond length in H_2 (where $\theta = 0$), $\langle S^2 \rangle = 0$ while, as the bond lengthens beyond r_{crit} (and θ monotonically approaches $\pi/4$), $\langle S^2 \rangle$ tends toward unity, i.e., the UHF wave function becomes, asymptotically, an equal mixture of singlet and triplet states.

It is interesting to study the expression for the UHF wave function given in Eq. (3.5) a little more closely. We recall that the exact wave function Eq. (3.1) is derived from the RHF wave function (R) by the addition of some of the RHF doubly excited determinant (C). Likewise, in forming the UHF wave function (U) from the RHF wave function (R), the RHF double excitation (C) is permitted to mix in,

$$\begin{bmatrix} R \\ A \\ B \\ C \end{bmatrix} = \begin{bmatrix} \cos^2 \theta & -\sin \theta \cos \theta & \sin \theta \cos \theta \\ \sin \theta \cos \theta & \cos^2 \theta & \sin^2 \theta \\ -\sin \theta \cos \theta & \sin^2 \theta & \cos^2 \theta \\ -\sin^2 \theta & -\sin \theta \cos \theta & \sin \theta \cos \theta \end{bmatrix} \begin{bmatrix} -\sin^2 \theta \\ \sin \theta \cos \theta \\ -\sin \theta \cos \theta \\ \cos^2 \theta \end{bmatrix} \begin{bmatrix} U \\ A' \\ B' \\ C' \end{bmatrix} \quad (4.1)$$

Using Eq. (4.1), it follows that the exact wave function

$$\begin{aligned} \Psi_{\text{exact}} &= R - \mu C \\ &= U(\cos^2 \theta + \mu \sin^2 \theta) - C'(\sin^2 \theta + \mu \cos^2 \theta) \\ &\quad + (B' - A')(1 - \mu) \sin \theta \cos \theta. \end{aligned} \quad (4.2)$$

Thus, when $r_{\text{crit}} < r < \infty$ (and therefore $0 < \theta < \pi/4$ and $0 < \mu < 1$), both the UHF singles (A' and B') and the UHF double (C') mix with the Hartree–Fock wave function (U) in forming the exact wave function. In contrast, at infinite separation ($\theta = \pi/4$, $\mu = 1$), the factor $(1 - \mu)$ vanishes and the UHF singles are *not* present in the exact wave function. Thus, the contribution from singles first rises as the bond is stretched beyond r_{crit} but eventually falls again, reaching zero at the point of complete dissociation and demonstrating that, even in the UHF framework, the exact wave function at infinite separation involves the admixture of *only* the doubly excited determinant to the Hartree–Fock determinant. By using Eq. (3.3) to express these two determinants in terms of the RHF determinants:

$$U(r = \infty) = (A - B) / \sqrt{2} + (R - C) / \sqrt{2}, \quad (4.3a)$$

$$C'(r = \infty) = (A - B) / \sqrt{2} - (R - C) / \sqrt{2}, \quad (4.3b)$$

even though UHF is only a single-determinant treatment. However, this mixing comes at the cost of contamination by the (higher-lying) triplet ($A - B$). The mixing will thus occur only when incorporation of the double excitation is particularly favorable (and contamination by the triplet not particularly unfavorable), i.e., when the separation between ψ_o and ψ_u is sufficiently small. Thus, *if it is energetically favorable, the (desirable) doubly excited and (undesirable) triplet RHF configuration state functions will mix into the RHF wave function to form a substantially spin-contaminated UHF wave function.* This conclusion will have important ramifications in our discussions of the HCC and CN radicals (Sec. VI).

IV. THE FULL-CI DESCRIPTIONS OF H_2 (MINIMAL BASIS SET)

In order to understand the way in which the UHF determinants contribute to the exact wave function, it is useful to begin by inverting the orthogonal matrix relation Eq. (3.3), thereby expressing the RHF orbitals in terms of the UHF orbitals. This is achieved by changing θ to $-\theta$ in the transformation matrix, thus:

it becomes clear that $(U - C') / \sqrt{2}$ will contain no triplet contaminant and is equal to the exact wave function.

The UHF and UCI (minimal basis set) treatments of H_2 as it is stretched from equilibrium ($r = r_{\text{eq}}$), past the onset of UHF instability ($r = r_{\text{crit}}$), and on to infinite separation ($r = \infty$) may be summarized as follows. Initially, near $r = r_{\text{eq}}$, the UHF and RHF wave functions are identical, $\langle S^2 \rangle = 0$, and only the double excitation mixes with the UHF wave function in the UCI (exact) wave function (Table I, $r = 0.75 \text{ \AA}$). As r becomes greater than r_{crit} (which, for H_2 with the STO-3G basis set, is 1.153 \AA), it becomes favorable for the RHF double and the unwanted RHF triplet contaminant to contribute to the UHF wave function Eq. (3.5) and, as a result, the UHF energy becomes lower than the RHF energy. Consequently, $\langle S^2 \rangle$ begins to increase. At this stage, both singly and doubly excited UHF determinants contribute to the UCI wave function (Table I, $r = 1.35 \text{ \AA}$). Eventually (at infinite separation), the UHF wave function becomes an equal mixture of singlet and triplet states and $\langle S^2 \rangle = 1$. However, the singles have again vanished from the UCI wave function, which is now a mixture of only the UHF ground and doubly excited determinants (Table I, $r = 2.50 \text{ \AA}$). This behavior, together with that of the analogous RHF and RCI descriptions, is concisely represented in Fig. 3.

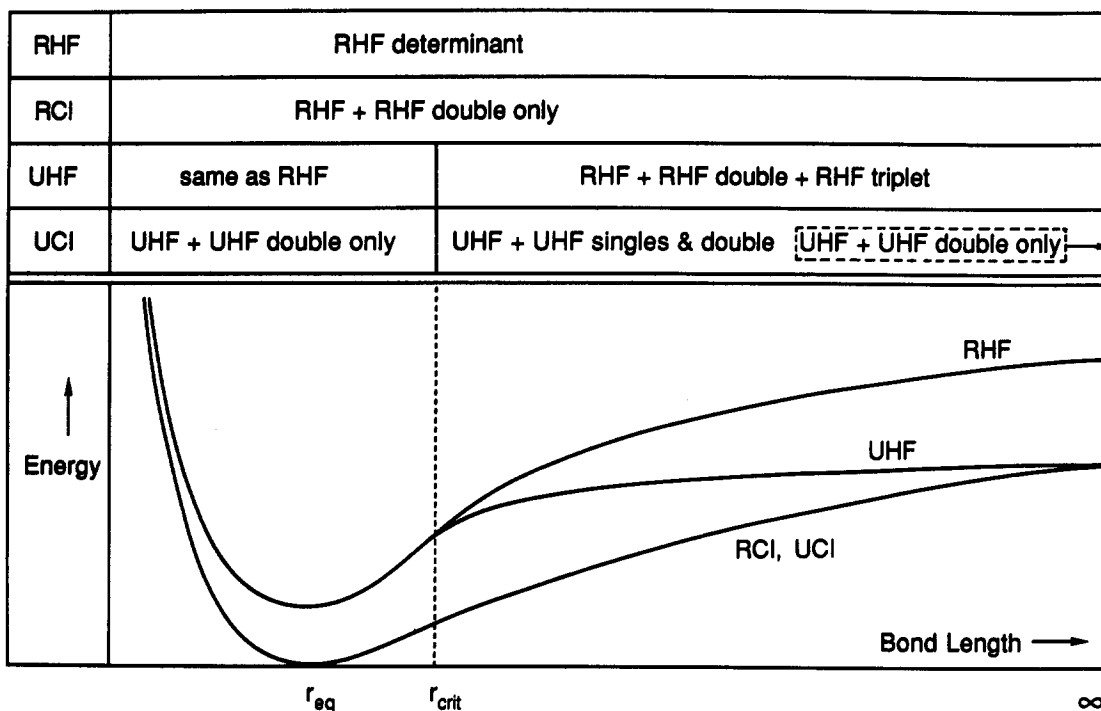


FIG. 3. The contributions to the RHF, RCI, UHF, and UCI wave functions for H_2 , using a minimal basis set.

V. THE UMP DESCRIPTION OF H_2 (MINIMAL BASIS SET)

A. Empirical observations and an approximate expression for the radius of convergence of the UMP λ parameter

It is interesting at this point to consider the bond length dependence of the rate of convergence of the UMP series (Table I). Near $r = r_{eq}$, where $UHF = RHF$ and $UMP = RMP$, convergence is rapid, 96% of the correlation energy (of 21 mhartree) being recovered at the UMP4 level. In contrast, at $r = 1.35 \text{ \AA}$, where $\langle S^2 \rangle = 0.49$, UMP4 recovers only a third of the available correlation energy (of 50 mhartree). This is reminiscent of the poor performance of UMP4 in treating the He_2^+ dication at its transition structure.⁴ The situation becomes even worse as the bond lengthens further still and $\langle S^2 \rangle$ tends toward unity. When $r = 2.00 \text{ \AA}$, UMP4 theory recovers less than 3% of the total correlation energy (of 11 mhartree) while, at $r = 2.50 \text{ \AA}$, only 0.4% (of 2 mhartree) is recovered. The additional observation that the UCI singles coefficient *drops* from 0.268 at $r = 1.35 \text{ \AA}$ to 0.094 at $r = 2.50 \text{ \AA}$ suggests that the slow convergence of the UMP series at long bond lengths is *not* due to the single excitations in the UCI wave function. We conclude, therefore, that the contribution of the UCI *double* excitation is not described well by low orders of MP theory.

Recently, Gill *et al.* have used a two-orbital, two-electron, doubles-only (" 2×2 ") model⁸ to derive an approximate formula for the radius of convergence Λ of the RMP λ parameter for a singlet species:

$$\Lambda(\psi_o, \psi_u) = (\epsilon_u - \epsilon_o)(\alpha^2 + K^2)^{-1/2}, \quad (5.1)$$

where the occupied (ψ_o) and unoccupied (ψ_u) molecular orbitals in the model have orbital energies ϵ_o and ϵ_u , respec-

tively, and the parameters α and K , which are related to elements of the 2×2 CID matrix, are combinations of Coulomb and exchange integrals (vide infra). They have shown that the corresponding RMP series is convergent if $\Lambda > 1$ and divergent otherwise. More specifically, they propose that the *rate* of convergence increases with increasing Λ . This implies that values of Λ only a little greater than unity will correspond to very slowly convergent MP series. The formalism which they used in deriving Eq. (5.1) for the RMP(2×2) series applies equally to the analogous UMP(2×2) series. Thus, by using the *unrestricted* Hartree–Fock values of ϵ_u , ϵ_o , α , and K in Eq. (3.10), we may deduce the approximate radius of convergence Λ of the UMP perturbation expansion for a singlet. The values for H_2 at various bond lengths are listed in the last column of Table I and are entirely consistent with the rates of convergence observed in the earlier columns of the table. This suggests that the main factors determining the convergence characteristics of the UMP expansion are contained within the two-orbital, two-electron model.

We propose, therefore, that the poor description afforded by UMP theory of the amplitude of the double excitation in the UCI wave function is responsible for the slow convergence of the UMP perturbation series for stretched H_2 . Moreover, we should emphasize that, for a general molecule, because determinants of other levels of excitation (i.e., singles, triples, quadruples, etc.) interact with the Hartree–Fock determinant only *through* the doubles, it is likely that *any determinant which interacts with the Hartree–Fock determinant through a poorly described double will, itself, also be poorly described*. For this reason, for example, the UCI singles contribution (25 mhartree) in stretched H_2 ($r = 1.35 \text{ \AA}$) is, like the doubles contribution (25 mhartree), very slowly introduced by successive orders of UMP

theory (Table I). Thus, even where the *direct* correlation contribution from a given doubly excited determinant is rather small, unsatisfactory convergence of a disproportionately large fraction of the total correlation energy of the system may result if that determinant is poorly described.

B. Asymptotic convergence behavior

It is important, in order to understand the origin of the unsatisfactory treatment afforded by UMP theory of the contributions of certain UHF doubles, to examine in more detail the Møller–Plesset expansion of the UCID energy for minimal-basis-set H_2 . Electron correlation is introduced through the exchange integral K_{ou} (between the occupied and unoccupied molecular orbitals ψ_o^α and ψ_u^α), which occurs as the off-diagonal element of the 2×2 CID correlation matrix⁴

$$\mathbf{H}_{\text{corr}} = \begin{bmatrix} 0 & K_{ou} \\ K_{ou} & 2\alpha - 2/x \end{bmatrix}, \quad (5.2a)$$

$$x = (\epsilon_o - \epsilon_u)^{-1}, \quad (5.2b)$$

$$\alpha = \frac{1}{2} (J_{oo} + J_{uu}) - 2J_{ou} + K_{ou}, \quad (5.2c)$$

where ϵ and J represent the usual orbital energies and Coulomb integrals, respectively. Clearly, if $K_{ou} = 0$, the correlation energy is zero. Because the doubly excited determinant is always higher in energy than the Hartree–Fock determinant (except at $r = \infty$, where they become degenerate), it follows from a comparison of the diagonal elements of (5.2a) that

$$\alpha x < 1 \quad \text{for } r < \infty, \quad (5.3a)$$

$$\alpha x = 1 \quad \text{for } r = \infty. \quad (5.3b)$$

The UHF exchange integral K_{ou}^{UHF} may be expressed in terms of the RHF molecular integrals using Eq. (3.2a) and thence may be related to $\langle S^2 \rangle_{\text{UHF}}$ using Eq. (3.6), thus

$$\begin{aligned} K_{ou}^{\text{UHF}} &= \int \int \psi_o^\alpha(1) \psi_u^\alpha(2) r_{12}^{-1} \psi_o^\alpha(2) \psi_u^\alpha(1) dV_1 dV_2 \\ &= K_{ou}^{\text{RHF}} (\cos^2 \theta - \sin^2 \theta)^2 + (J_{oo}^{\text{RHF}} + J_{uu}^{\text{RHF}} \\ &\quad - 2J_{ou}^{\text{RHF}}) \sin^2 \theta \cos^2 \theta = (1 - \langle S^2 \rangle_{\text{UHF}}) K_{ou}^{\text{RHF}} \\ &\quad + (J_{oo}^{\text{RHF}} - J_{uu}^{\text{RHF}} - 2J_{ou}^{\text{RHF}}) \langle S^2 \rangle_{\text{UHF}} / 4. \end{aligned} \quad (5.4)$$

As the bond length in H_2 is increased beyond r_{crit} , the factors $(J_{oo}^{\text{RHF}} + J_{uu}^{\text{RHF}} - 2J_{ou}^{\text{RHF}})$ and $(1 - \langle S^2 \rangle_{\text{UHF}})$ in Eq. (5.4) decay exponentially while $2K_{ou}^{\text{RHF}}$ and $\langle S^2 \rangle$ tend toward the one-center two-electron repulsion integral¹³ and unity [Eq. (3.6)], respectively. As a result, from Eq. (5.4), K_{ou}^{UHF} decays exponentially.

Gill *et al.* have derived⁴ the following recursion formula for the n th-order term E_n in the Møller–Plesset expansion of the lower eigenvalue of Eq. (5.2a):

$$E_n = x \left[\alpha E_{n-1} - \frac{1}{2} (E_2 E_{n-2} + \cdots + E_{n-2} E_2) \right], \quad n > 2 \quad (5.5a)$$

$$E_2 = K_{ou}^2 x / 2. \quad (5.5b)$$

We can transform Eq. (5.5) to a canonical form by introducing

$$P_n(t) = P_{n-1}(t) - t [P_0(t)P_{n-2}(t) + \cdots + P_{n-2}(t)P_0(t)], \quad n > 0 \quad (5.6a)$$

$$P_0(t) \equiv 1. \quad (5.6b)$$

The function P_n is an $[n/2]$ th degree polynomial of the form

$$P_n(t) = 1 - \frac{1}{2} n(n-1)t + \dots \quad (5.7)$$

It can now be verified, by substitution into Eq. (5.5), that

$$E_n = (2t/x)(\alpha x)^n P_{n-2}(t) \quad (5.8a)$$

$$t = K_{ou}^2 / 4\alpha^2. \quad (5.8b)$$

Moreover, because K_{ou}^{UHF} vanishes exponentially as $r \rightarrow \infty$ while α tends toward a nonzero value, it follows from Eq. (5.8b) that, as r increases, t^{UHF} decays exponentially toward zero. Consequently, for large r , *within the UHF framework*

$$P_n(t) \simeq 1 \quad (5.9)$$

and

$$E_n \simeq (2t/x)(\alpha x)^n. \quad (5.10)$$

Thus, when the bond is sufficiently stretched that K_{ou}^{UHF} is small, the sequence $\{E_n^{\text{UHF}}\}$ is approximately geometric. Furthermore, it follows from Eq. (5.3) that the geometric series, although convergent for $r < \infty$, converges increasingly slowly with increasing bond length because αx tends to unity. We conclude, therefore, that the minimal-basis-set UMP series for the UCID energy of stretched H_2 is an approximately geometric series whose rate of convergence deteriorates (although there is less correlation energy to recover) as the bond length is increased.

At this point, it is useful to summarize our findings for the stretched H_2 molecule with a minimal basis set. We consider the case where $r_{\text{crit}} \ll r < \infty$. In the (spin-restricted) RHF framework, only two determinants (R and the doubly excited determinant C in Fig. 1) contribute to the RCI (exact) wave function and the matrix element K_{ou}^{RHF} between them (and the correlation energy) is large. In the UHF framework, the situation is very different. Because the spin restriction has been removed, both the RHF double excitation C and the RHF triplet $(A-B)\sqrt{2}$ contribute to the UHF determinant U , the UHF molecular orbitals (Fig. 2) break symmetry, and the UHF wave function is spin polarized. The UHF wave function is lower in energy than the RHF wave function but it is spin contaminated (by the RHF triplet). In this case, the matrix element K_{ou}^{UHF} between the ground and doubly excited UHF determinants (U and C' in Fig. 2) is considerably smaller (than K_{ou}^{RHF}) and, as a consequence, the UMP series is only slowly convergent.

VI. THE CYANO AND ETHYNYL RADICALS

We are now in a position to discuss the poor UMP convergence of the isoelectronic HCC \cdot and CN \cdot radicals (Tables II and III). The molecular orbital scheme for both of these molecules is depicted in Fig. 4. Both species are σ radicals in which the unpaired electron is strongly localized. If the restricted (ROHF) and unrestricted (UHF) determinants for these radicals are enumerated and related to one another (as we did for H_2), the transformation matrix

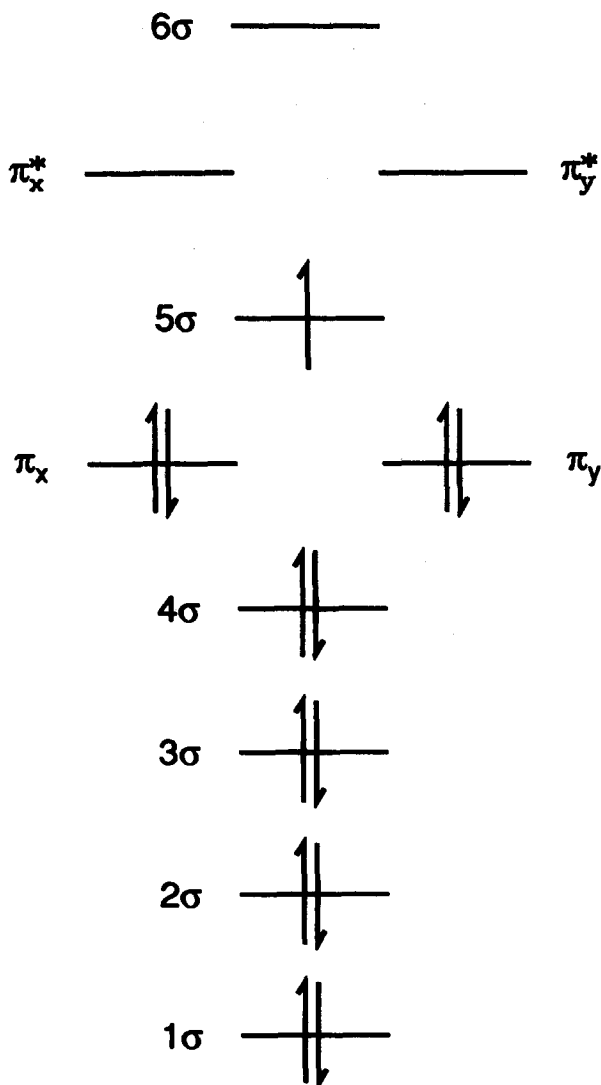


FIG. 4. The molecular orbital scheme for the CN^\cdot and HCC^\cdot radicals. The HCC^\cdot radical has, in addition, a high-lying 7σ orbital.

between the ROHF and UHF determinants involving $\pi_x \rightarrow \pi_x^*$ (or, equivalently, $\pi_y \rightarrow \pi_y^*$) excitations is identical to that in Eq. (3.3), derived above for H_2 . From inspection of Fig. 4, we would expect that the doubly excited determinant in which both π_x electrons are promoted to π_x^* (or, equally, that in which both π_y electrons are promoted to π_y^*) should be important in these systems because the $\pi \rightarrow \pi^*$ separation is small. However, in both of these species, the localization of the unpaired α electron leads, within the UHF description, to substantial spin polarization in the π -electron framework, i.e., one end of the molecule has an excess of α π -electron density while, at the other end, there is a corresponding excess of β π -electron density. In this respect, there is an analogy between the equilibrium HCC^\cdot and CN^\cdot radicals and the stretched H_2 molecule (in which the spin polarization is in the σ framework). Furthermore, the π spin polarization in these radicals manifests itself exactly as the σ spin polarization does in stretched H_2 , i.e., the UHF wave function is significantly spin contaminated ($\langle S^2 \rangle_{\text{UHF}}$, which is 0.75 for a pure doublet wave function, is 1.564 for CN^\cdot and 1.358 for HCC^\cdot , at the geometries used).

In Tables II and III, we examine the convergence behavior of the UMP series within a variety of post-SCF windows in CN^\cdot and HCC^\cdot , respectively. For both radicals, the frozen-core UMP series converge poorly, only 65.7% and 77.0%, respectively, of the correlation energy being recovered even by fourth-order MP theory. The drastic consequences of such slow convergence on the calculated electron affinity¹⁴ of the CN^\cdot radical and on the H–C bond dissociation energy of HCN have been discussed⁵ by Nobes *et al.* The UCISD amplitude for the $\pi_x \rightarrow \pi_x^*$ singly excited determinant (0.168 for CN^\cdot and 0.123 for HCC^\cdot) is significant in both species and, like the analogous UHF singles in the stretched H_2 system (Table I), is probably necessary to remove the spin contamination in the underlying UHF wave function. In the case of CN^\cdot , the $4\sigma \rightarrow 5\sigma$ single is also found to contribute significantly (0.138) to the UCISD wave function.

When the UMP and full-CI energies of CN^\cdot and HCC^\cdot are calculated within a smaller post-SCF window, consisting of the π_x , 5σ , and π_x^* molecular orbitals (Fig. 4), the rates of convergence of the resulting UMP series and the amplitudes of the $\pi_x \rightarrow \pi_x^*$ single and double excitations are similar to those found using the frozen-core window. In contrast, the convergence of the UMP series within the $\{4\sigma, 5\sigma, \pi_x^*\}$ window (where the $\pi \rightarrow \pi^*$ excitations are excluded) is much more satisfactory, MP4 recovering most (91.1% for CN^\cdot and 93.8% for HCC^\cdot) of the available correlation energy. Moreover, in the larger $\{4\sigma, \pi_x, 5\sigma, \pi_x^*\}$ window, the convergence is again poor, strongly resembling that in the $\{\pi_x, 5\sigma, \pi_x^*\}$ window. These striking comparisons are consistent with the proposal that, just as the poorly described doubly excited UHF determinant (C') was responsible for the slow UMP convergence in stretched H_2 , the poor convergence in CN^\cdot and HCC^\cdot results from an inadequate treatment of the $\pi_x \rightarrow \pi_x^*$ (and $\pi_y \rightarrow \pi_y^*$) doubly excited determinants. We note, additionally, that the important $4\sigma \rightarrow 5\sigma$ single in CN^\cdot apparently mixes with the Hartree–Fock determinant largely through the $\pi \rightarrow \pi^*$ doubles for, when the π_x molecular orbital is added to the $\{4\sigma, 5\sigma, \pi_x^*\}$ window, the $4\sigma \rightarrow 5\sigma$ amplitude increases dramatically to approximately its frozen-core value. Presumably, the correlation contribution from any determinant which, like this one, interacts through the problematic $\pi \rightarrow \pi^*$ doubles will be only slowly introduced by successive orders of MP theory.

We would propose that *spin contamination will generally be significant in the UHF wave functions of radicals for which a low-lying double excitation is possible*. For such systems, the UMP series are likely to display poor convergence.

VII. CONCLUSIONS

In this paper, we have proposed that the slow convergence of the UMP series for stretched H_2 and for the CN^\cdot and HCC^\cdot radicals may be traced, in each case, to the failure of UMP theory to treat satisfactorily systems with important, low-lying, doubly excited determinants. In the RHF (or ROHF) framework, such determinants have large (RCI) matrix elements with the Hartree–Fock determinant. However, when the spin restriction is relaxed, the energy is lowered significantly, the resulting UHF wave function is substantially spin polarized (leading to spin contamina-

tion), and the (UCI) matrix elements are considerably smaller. By demonstrating that the rate of MP convergence decreases as these matrix elements become smaller we have rationalized earlier proposals that spin contamination and poor UMP convergence are related. Our findings suggest that, in general, species for which low-lying double excitations are possible (e.g., systems containing homolytically cleaving bonds and most unsaturated radicals) are likely to suffer from such poor convergence.

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