

Analytical gradients for unrestricted Hartree–Fock and second order Møller–Plesset perturbation theory with single spin annihilation

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Unrestricted Hartree–Fock (UHF) wave functions and Møller–Plesset perturbation theory (UMPn) based on a single spin-unrestricted reference determinant can contain significant contamination from unwanted spin states. This contamination may lead to large distortions of the potential energy surface, particularly at the UMPn level. A simple approximation to projected UMPn theory (PMPn) improves the shape of the potential energy surface significantly. Formulas for analytical gradients of the PUHF and approximate projected UMP2 energies with single annihilation have been derived and programmed. This code has been applied to the optimization of transition states for $\text{H} + \text{C}_2\text{H}_4$, $\text{H} + \text{CH}_2\text{O}$ and $\text{H} + \text{C}_2\text{H}_2$ at the PMP2/6-31G* level.

INTRODUCTION

Spin-unrestricted Hartree–Fock¹ (UHF) calculations and unrestricted Møller–Plesset perturbation theory² are usually quite reliable for open shell systems and yield reasonable energetics and optimized geometries. However, if spin contamination is significant, the unwanted spin states can distort the energy surface significantly, especially when electron correlation corrections are treated by Møller–Plesset perturbation theory. Spin-projection methods offer one approach for overcoming the difficulties caused by spin contamination.^{3–6} These methods are based on the Löwdin spin-projection operator⁴ or the corresponding spin-annihilation operators

$$\hat{P}_s = \prod_{k \neq s} \frac{\hat{S}^2 - k(k+1)}{s(s+1) - k(k+1)}, \quad (1)$$

$$\hat{A}_k = \frac{\hat{S}^2 - k(k+1)}{s(s+1) - k(k+1)}.$$

Early work focused on spin-projected unrestricted Hartree–Fock (PUHF) and spin-extended Hartree–Fock (EHF) methods.^{3–6} Recent work has examined the use of spin-projection and spin-annihilation methods to improve energies at the MPn level.^{7–10} The simplest approximation to spin-projected Møller–Plesset perturbation theory,⁷ denoted by PMPn, involves the annihilation of the largest spin contaminant in the UHF wave function, followed by a correction for the configurations already in the UMP1 to UMPn-1 wave functions. This approximation was used successfully in a number of studies.^{7,11–14} Subsequently, formulas for full spin-projected UMPn were developed,^{9,10} and calculations confirmed that the initial approximate method yields satisfactory results when the contamination is dominated by a single higher spin.

In this paper, the formulas for analytical gradients of the PUHF energy and the PMP2 energy with single annihilation are derived. These equations have been programmed and interfaced with the development version GAUSSIAN 88 series of programs.¹⁵ Initial timings suggest that little extra effort is required than for UMP2 derivatives. The analytical PMP2

gradients have been applied to the optimization of the transition states for $\text{H} + \text{C}_2\text{H}_4$, $\text{H} + \text{CH}_2\text{O}$ and $\text{H} + \text{C}_2\text{H}_2$.

PUHF and PMP2 energies

The Hartree–Fock energy after annihilation of the next highest spin state is given by

$$\frac{\langle \Phi_0 | \hat{H} | \hat{A}_{s+1} \Phi_0 \rangle}{\langle \Phi_0 | \hat{A}_{s+1} \Phi_0 \rangle} = E_{\text{UHF}} + \langle \Phi_0 | \hat{V} | \tilde{\Phi}_0 \rangle$$

$$= E_{\text{UHF}} + \sum_i^{sd} \frac{\langle \Phi_0 | \hat{V} | \Psi_i \rangle \langle \Psi_i | \hat{S}^2 | \Phi_0 \rangle}{\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s+1)(s+2)}$$

$$= E_{\text{UHF}} + \Delta E_{\text{PUHF}}, \quad (2)$$

where \hat{A}_{s+1} is the operator which annihilates states with spin $s+1$, \hat{V} is the usual Møller–Plesset perturbation operator and Φ_0 is the UHF reference determinant. The correction for spin annihilation of states with spin $s+1$, $\tilde{\Phi}_0$, is given by

$$|\tilde{\Phi}_0\rangle = \sum_i^{sd} \frac{|\Psi_i\rangle \langle \Psi_i | \hat{S}^2 | \Phi_0 \rangle}{\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s+1)(s+2)}. \quad (3)$$

The summation in Eq. (3) runs over all singly and doubly excited determinants. The MP2 energy and the first order wave function Φ_1 are

$$E_{\text{UMP2}} = E_{\text{UHF}} - \sum_i^d \langle \Psi_i | \hat{V} | \Phi_0 \rangle^2 / (E_i - E_0), \quad (4)$$

$$|\Phi_1\rangle = - \sum_i^d |\Psi_i\rangle \langle \Psi_i | \hat{V} | \Phi_0 \rangle / (E_i - E_0). \quad (5)$$

As a first approximation to the spin projected MP2 energy, the correction for spin contamination at the UHF level, $\tilde{\Phi}_0$, must be reduced by the fraction contained in Φ_1 . With this approximation, the PMP2 energy may be written as

$$E_{\text{PMP2}} = E_{\text{UMP2}} + \Delta E_{\text{PUHF}} (1 - \langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle). \quad (6)$$

This approximation has been used successfully in a number of studies.^{7,11–14}

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PUHF gradients

The first derivative of the PUHF energy can be written as

$$E_{\text{PUHF}}^X = E_{\text{UHF}}^X + \Delta E_{\text{PUHF}}^X. \quad (7)$$

The superscript X is used to indicate differentiation with respect to X . The expression for the first derivative of the Hartree–Fock energy is well-known.¹⁶

The derivative of ΔE_{PUHF} is given by

$$\begin{aligned} \Delta E_{\text{PUHF}}^X &= \sum_{ijab} \{ \langle \Phi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle^X \langle \Psi_{ij}^{ab} | \hat{S}^2 | \Phi_0 \rangle \\ &\quad + \langle \Phi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle \langle \Psi_{ij}^{ab} | \hat{S}^2 | \Phi_0 \rangle^X \} \Omega^{-1} \\ &\quad - \Delta E_{\text{PUHF}} \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle^X \Omega^{-1}, \end{aligned} \quad (8)$$

where

$$\Omega = [\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s+1)(s+2)] \quad (9)$$

and Ψ_{ij}^{ab} denotes a doubly excited determinant in which the electrons from occupied orbitals i and j are promoted to virtual orbitals a and b .

To simplify the notation, a number of conventions are adopted: indices i, j, k, l , etc. are used for occupied orbitals; a, b, c, d , etc. denote virtual orbitals and p, q, r , etc. refer to either set. For cases where it is necessary to distinguish spin, indices i, k , etc. and a, c , etc. are used for alpha spin and indices j, l , etc. and b, d , etc. are used for beta spin. Greek letters refer to the atomic orbital basis functions. The α – β overlap integrals are denoted as \tilde{S}_{ij} with the convention that all pairs of integral indices have the α label first and the β label second.

The expectation value of \hat{S}^2 and its derivative are given by

$$\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle = s_z^2 + s_z + n_\beta - \sum_{ij} \tilde{S}_{ij}^2, \quad (10)$$

$$\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle^X = -2 \sum_{ij} \tilde{S}_{ij} \tilde{S}_{ij}^X, \quad (11)$$

where n_β is the number of beta electrons and

$$\begin{aligned} \tilde{S}_{ij}^X &= \sum_{\mu\nu} C_{\mu i}^X S_{\mu\nu} C_{\nu j} + C_{\mu i} S_{\mu\nu}^X C_{\nu j} + C_{\mu i} S_{\mu\nu} C_{\nu j}^X \\ &= \sum_p U_{ip} \tilde{S}_{pj} + \tilde{S}_{ij}^{(X)} + \sum_p \tilde{S}_{ip} U_{pj} \end{aligned} \quad (12)$$

and

$$\frac{\partial C_{\mu q}}{\partial X} = C_{\mu q}^X = \sum_p C_{\mu p} U_{pq}. \quad (13)$$

The $C_{\mu q}$ refer to the unperturbed UHF orbital coefficients and the U_{pq} are the first order orbital coefficients obtained from the solution of the coupled perturbed Hartree–Fock (CPHF) equations.^{17,18} A superscript X in parentheses indicates an integral derivative evaluated in the atomic orbital basis and transformed by the unperturbed orbital coefficients [e.g., $\tilde{S}^{(X)}$ in Eq. (12)].

The matrix elements of \hat{S}^2 between the ground and $\alpha\beta$ doubly excited configurations Ψ_{ij}^{ab} can be written as

$$\langle \Phi_0 | \hat{S}^2 | \Psi_{ij}^{ab} \rangle = -\tilde{S}_{ib} \tilde{S}_{aj}. \quad (14)$$

The derivatives of these matrix elements are

$$\langle \Phi_0 | \hat{S}^2 | \Psi_{ij}^{ab} \rangle^X = -\tilde{S}_{ib}^X \tilde{S}_{aj} - \tilde{S}_{ib} \tilde{S}_{aj}^X. \quad (15)$$

In the same notation, the derivatives of the integrals of \hat{V} between the ground and doubly excited configurations are given by

$$\begin{aligned} \langle \Phi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle^X &= (ij||ab)^X \\ &= (ij||ab)^{(X)} + \sum_p [(pj||ab) U_{pi} + (ip||ab) U_{pj} \\ &\quad + (ij||pb) U_{pa} + (ij||ap) U_{pb}], \end{aligned} \quad (16)$$

where

$$(ij||ab)^{(X)} = \sum_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu j} C_{\lambda a} C_{\sigma b} (\mu\nu||\lambda\sigma)^X. \quad (17)$$

Substituting Eqs. (11)–(17) into Eq. (8) gives

$$\begin{aligned} \Delta E_{\text{PUHF}}^X &= - \sum_{ijab} \left\{ (ij||ab)^{(X)} + \sum_p [(pj||ab) U_{pi} \right. \\ &\quad + (ip||ab) U_{pj} + (ij||pb) U_{pa} + (ij||ap) U_{pb}] \tilde{S}_{ib} \tilde{S}_{aj} \\ &\quad + (ij||ab) \sum [(U_{ip} \tilde{S}_{pb} + \tilde{S}_{ib}^{(X)} + \tilde{S}_{ib} U_{pb}) \tilde{S}_{aj} \\ &\quad + \tilde{S}_{ib} (U_{ap} \tilde{S}_{pj} + \tilde{S}_{aj}^{(X)} + \tilde{S}_{ap} U_{pj})] \left. \right\} \Omega^{-1} \\ &\quad + 2 \Delta E_{\text{PUHF}} \sum [U_{kp} \tilde{S}_{pl} + \tilde{S}_{kl}^{(X)} + \tilde{S}_{kp} U_{pl}] \tilde{S}_{kl} \Omega^{-1}. \end{aligned} \quad (18)$$

This expression can be simplified by noting that only the symmetric part of the occupied–occupied and virtual–virtual blocks of U are needed. These can be obtained from the orbital orthogonality condition:

$$\begin{aligned} \sum_{\mu\nu} C_{\mu i}^X S_{\mu\nu} C_{\nu k} + C_{\mu i} S_{\mu\nu}^X C_{\nu k} + C_{\mu i} S_{\mu\nu} C_{\nu k}^X \\ = U_{ik} + S_{ik}^{(X)} + U_{kj} = 0 \end{aligned} \quad (19)$$

or specifically for the α and β occupied–occupied and virtual–virtual blocks:

$$\begin{aligned} U_{ik} + U_{ki} = -S_{ik}^{(X)}, \quad U_{jl} + U_{lj} = -S_{jl}^{(X)}, \\ U_{ac} + U_{ca} = -S_{ac}^{(X)}, \quad U_{bd} + U_{db} = -S_{bd}^{(X)}. \end{aligned} \quad (20)$$

After collecting terms in $(\mu\nu||\lambda\sigma)^X$, the U 's and the various overlap derivatives, the final expression for the computation of the derivative of ΔE_{PUHF} with single annihilation is

$$\begin{aligned}
 \Delta E_{\text{PUHF}}^X &= \sum_{\mu\nu\lambda\sigma} \Gamma_{\mu\nu\lambda\sigma} (\mu\nu|\lambda\sigma)^X + \sum_{ic} U_{ci} \left\{ - \sum_{jab} [(cj||ab)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{cb}\tilde{S}_{aj}] + 2\Delta E_{\text{PUHF}} \sum_j \tilde{S}_{cj}\tilde{S}_{ij} \right\} \Omega^{-1} \\
 &+ \sum_{jd} U_{dj} \left\{ - \sum_{iab} [(id||ab)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{ib}\tilde{S}_{ad}] + 2\Delta E_{\text{PUHF}} \sum_i \tilde{S}_{id}\tilde{S}_{ij} \right\} \Omega^{-1} \\
 &+ \sum_{ak} U_{ka} \left\{ - \sum_{ijb} [(ij||kb)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{ib}\tilde{S}_{kj}] \right\} \Omega^{-1} \\
 &+ \sum_{bl} U_{lb} \left\{ - \sum_{ija} [(ij||al)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{il}\tilde{S}_{aj}] \right\} \Omega^{-1} \\
 &- \sum_{ik} S_{ki}^{(X)} \left\{ - \frac{1}{2} \sum_{jab} [(kj||ab)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{kb}\tilde{S}_{aj}] + \Delta E_{\text{PUHF}} \sum_j \tilde{S}_{kj}\tilde{S}_{ij} \right\} \Omega^{-1} \\
 &- \sum_{jl} S_{lj}^{(X)} \left\{ - \frac{1}{2} \sum_{iab} [(il||ab)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{ib}\tilde{S}_{al}] + \Delta E_{\text{PUHF}} \sum_i \tilde{S}_{il}\tilde{S}_{ij} \right\} \Omega^{-1} \\
 &- \sum_{ac} S_{ca}^{(X)} \left\{ - \frac{1}{2} \sum_{ijb} [(ij||cb)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{ib}\tilde{S}_{cj}] \right\} \Omega^{-1} \\
 &- \sum_{bd} S_{db}^{(X)} \left\{ - \frac{1}{2} \sum_{ija} [(ij||ad)\tilde{S}_{ib}\tilde{S}_{aj} + (ij||ab)\tilde{S}_{id}\tilde{S}_{aj}] \right\} \Omega^{-1} \\
 &+ \sum_{\mu\nu} S_{\mu\nu}^X \left\{ \sum_{jab} [-C_{\mu i} C_{\nu b} (ij||ab)\tilde{S}_{aj} - C_{\mu a} C_{\nu j} (ij||ab)\tilde{S}_{ib}] + 2\Delta E_{\text{PUHF}} \sum_{ij} C_{\mu i} C_{\nu j} \tilde{S}_{ij} \right\} \Omega^{-1}, \tag{21}
 \end{aligned}$$

where

$$\Gamma_{\mu\nu\lambda\sigma} = - \sum_{ijab} C_{\mu i} C_{\nu j} C_{\lambda a} C_{\sigma b} \tilde{S}_{ib} \tilde{S}_{aj} \Omega^{-1}. \tag{22}$$

This completes the derivation of the PUHF gradients for single annihilation. As can be seen by comparison with Ref. 18, the terms are very similar to the MP2 gradients.

PMP2 gradients

For the evaluation of PMP2 derivatives it is necessary to obtain derivatives of the term $[\langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle]$ in addition to the derivatives of E_{UMP2} and ΔE_{PUHF} .

$$\begin{aligned}
 E_{\text{PMP2}}^X &= E_{\text{UMP2}}^X + \Delta E_{\text{PUHF}}^X (1 - \langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle) \\
 &- \Delta E_{\text{PUHF}} (\langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle)^X, \tag{23}
 \end{aligned}$$

$$\begin{aligned}
 &[\langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle]^X \\
 &= [\langle \Phi_1 | \tilde{\Phi}_0 \rangle^X / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle] \\
 &- \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle^X [\langle \Phi_1 | \tilde{\Phi}_0 \rangle / \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle^2]. \tag{24}
 \end{aligned}$$

The numerator on the left-hand side of Eq. (24) can be written as

$$\begin{aligned}
 \langle \Phi_1 | \tilde{\Phi}_0 \rangle &= - \sum_i \langle \Phi_0 | \hat{V} | \Psi_i \rangle \langle \Psi_i | \hat{S}^2 | \Phi_0 \rangle [(E_i - E_0)\Omega]^{-1} \\
 &= \sum_{ijab} (ij||ab) \tilde{S}_{ib} \tilde{S}_{aj} (\Delta_{ijab} \Omega)^{-1}, \tag{25}
 \end{aligned}$$

where $\Delta_{ijab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$ and the ϵ 's are the orbital energies. Differentiation of Eq. (25) with respect to X gives

$$\begin{aligned}
 \langle \Phi_1 | \tilde{\Phi}_0 \rangle^X &= \sum_{ijab} \left\{ (ij||ab)^{(X)} \tilde{S}_{ib} \tilde{S}_{aj} (\Delta_{ijab})^{-1} + \sum_p [(pj||ab) U_{pi} + (ip||ab) U_{pj} + (ij||pb) U_{pa} \right. \\
 &+ (ij||ap) U_{pb}] \tilde{S}_{ib} \tilde{S}_{aj} (\Delta_{ijab})^{-1} + (ij||ab) \sum [(U_{ip} \tilde{S}_{pb} + S_{ib}^{(X)} + S_{ip} U_{pb}) \tilde{S}_{aj} \\
 &+ \tilde{S}_{ib} (U_{ap} \tilde{S}_{pj} + \tilde{S}_{aj}^{(X)} + \tilde{S}_{ap} U_{pj})] (\Delta_{ijab})^{-1} - (ij||ab) \tilde{S}_{ib} \tilde{S}_{aj} (\epsilon_a^X + \epsilon_b^X - \epsilon_i^X - \epsilon_j^X) (\Delta_{ijab})^{-2} \left. \right\} \Omega^{-1} \\
 &- 2 \langle \tilde{\Phi}_0 | \Phi_1 \rangle \sum [U_{kp} \tilde{S}_{pl} + \tilde{S}_{kl}^{(X)} + \tilde{S}_{kp} U_{pl}] \tilde{S}_{kl} \Omega^{-1}. \tag{26}
 \end{aligned}$$

The orbital energy derivatives ϵ_p^X can be obtained from the first order Fock matrix, which in turn may be assembled from the solution of the CPHF equations. In addition to the symmetric part of the occupied-occupied and virtual-virtual blocks of U_{pq} [Eq. (20)], a little algebra reveals that the antisymmetric part of the occupied-occupied and virtual-virtual blocks of U multiplied by orbital energy differences [e.g., $(\epsilon_q - \epsilon_p) (U_{pq} - U_{qp})$] are also needed to evaluate Eq. (26). These can also be obtained from the CPHF equations:

$$F_{\mu\nu}^X C_{\nu q} + F_{\mu\nu} C_{\mu q}^X = \epsilon_q^X S_{\mu\nu} C_{\nu q} + \epsilon_q S_{\mu\nu}^X C_{\nu q} + \epsilon_q S_{\mu\nu} C_{\mu q}^X. \tag{27}$$

Note that $F_{\mu\nu}^{(X)}$ includes the derivative of the density matrix. To transform the CPHF equations to the molecular orbital basis, Eq. (27) is left multiplied by $C_{\mu p}$ and Eq. (12) is used to express the orbital coefficient derivatives in terms of the U 's:

$$F_{pq}^{(X)} + \epsilon_p U_{pq} = \epsilon_p^X \delta_{pq} + \epsilon_q S_{pq}^{(X)} + \epsilon_q U_{pq}. \quad (28)$$

As in Eqs. (12) and (17), the superscript (X) is used to denote the integral derivative in the atomic basis transformed by the unperturbed molecular orbitals. The antisymmetric part of U can be obtained by adding Eq. (28) to itself with the indices p and q permuted (note that $F_{pq}^{(X)}$ and $S_{pq}^{(X)}$ are symmetric)

$$\begin{aligned} (\epsilon_q - \epsilon_p)(U_{pq} - U_{qp})/2 &= F_{pq}^{(X)} - \frac{1}{2}(\epsilon_p + \epsilon_q)S_{pq}^{(X)} \\ &= \tilde{F}_{pq}^{(X)}. \end{aligned} \quad (29)$$

After Eq. (26) is rewritten in terms of the symmetric and antisymmetric parts of the occupied-occupied and virtual-virtual blocks of U , the final expression used to compute the derivative of $\langle \Phi_1 | \tilde{\Phi}_0 \rangle$ is

$$\begin{aligned} \langle \Phi_1 | \tilde{\Phi}_0 \rangle^X &= \sum_{\mu\nu\lambda\sigma} \Gamma'_{\mu\nu\lambda\sigma} (\mu\nu || \lambda\sigma)^X + \sum_{ic} U_{ci} \left\{ \sum_{jab} [(cj || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{cb} \tilde{S}_{aj}] / \Delta_{ijab} - 2 \langle \Phi_1 | \tilde{\Phi}_0 \rangle \sum_j \tilde{S}_{cj} \tilde{S}_{ij} \right\} \Omega^{-1} \\ &+ \sum_{jd} U_{dj} \left\{ \sum_{iab} [(id || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{ib} \tilde{S}_{ad}] / \Delta_{ijab} - 2 \langle \Phi_1 | \tilde{\Phi}_0 \rangle \sum_j \tilde{S}_{id} \tilde{S}_{ij} \right\} \Omega^{-1} \\ &+ \sum_{ak} U_{ka} \left\{ \sum_{ijb} [(ij || kb) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{ib} \tilde{S}_{kj}] / \Delta_{ijab} \right\} \Omega^{-1} \\ &+ \sum_{bl} U_{lb} \left\{ \sum_{ija} [(ij || al) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{il} \tilde{S}_{aj}] / \Delta_{ijab} \right\} \Omega^{-1} \\ &+ \sum_{ik} \tilde{F}_{ki}^{(X)} \left\{ -\frac{1}{2} \sum_{jab} [(kj || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{kb} \tilde{S}_{aj}] / (\Delta_{ijab} \Delta_{kjab}) \right\} \Omega^{-1} \\ &+ \sum_{jl} \tilde{F}_{lj}^{(X)} \left\{ -\frac{1}{2} \sum_{iab} [(il || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{il} \tilde{S}_{aj}] / (\Delta_{ijab} \Delta_{ilab}) \right\} \Omega^{-1} \\ &- \sum_{ac} \tilde{F}_{ca}^{(X)} \left\{ -\frac{1}{2} \sum_{ijb} [(ij || cb) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{ib} \tilde{S}_{cj}] / (\Delta_{ijab} \Delta_{ijcb}) \right\} \Omega^{-1} \\ &- \sum_{bd} \tilde{F}_{db}^{(X)} \left\{ -\frac{1}{2} \sum_{ija} [(ij || ad) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{id} \tilde{S}_{aj}] / (\Delta_{ijab} \Delta_{ijad}) \right\} \Omega^{-1} \\ &- \sum_{ik} S_{ki}^{(X)} \left\{ \frac{1}{2} \sum_{jab} [(kj || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{kb} \tilde{S}_{aj}] / \Delta_{ijab} - 2 \langle \tilde{\Phi}_0 | \Phi_1 \rangle \sum_j \tilde{S}_{kj} \tilde{S}_{ij} \right\} \Omega^{-1} \\ &- \sum_{jl} S_{lj}^{(X)} \left\{ \frac{1}{2} \sum_{iab} [(il || ab) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{il} \tilde{S}_{aj}] / \Delta_{ijab} - 2 \langle \tilde{\Phi}_0 | \Phi_1 \rangle \sum_j \tilde{S}_{il} \tilde{S}_{ij} \right\} \Omega^{-1} \\ &- \sum_{ac} S_{ca}^{(X)} \left\{ \frac{1}{2} \sum_{ijb} [(ij || cb) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{ib} \tilde{S}_{cj}] / \Delta_{ijab} \right\} \Omega^{-1} \\ &- \sum_{bd} S_{db}^{(X)} \left\{ \frac{1}{2} \sum_{ija} [(ij || ad) \tilde{S}_{ib} \tilde{S}_{aj} + (ij || ab) \tilde{S}_{id} \tilde{S}_{aj}] / \Delta_{ijab} \right\} \Omega^{-1} \\ &+ \sum_{\mu\nu} S_{\mu\nu}^X \left\{ \sum_{jab} [C_{\mu i} C_{\nu b} (ij || ab) \tilde{S}_{aj} + C_{\mu a} C_{\nu j} (ij || ab) \tilde{S}_{ib}] / \Delta_{ijab} - 2 \langle \Phi_1 | \tilde{\Phi}_0 \rangle \sum_{ij} C_{\mu i} C_{\nu j} \tilde{S}_{ij} \right\} \Omega^{-1}, \end{aligned} \quad (30)$$

where

$$\Gamma'_{\mu\nu\lambda\sigma} = \sum_{ijab} C_{\mu i} C_{\nu j} C_{\lambda a} C_{\sigma b} \tilde{S}_{ib} \tilde{S}_{aj} (\Delta_{ijab} \Omega)^{-1}. \quad (31)$$

Similar to ΔE_{PUHF}^X , the $\langle \Phi_1 | \tilde{\Phi}_0 \rangle^X$ term is closely related to the MP2 gradient.

Finally, it is necessary to evaluate the term $\langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle^X$. Analogously to Eq. (15), $\langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle$ may be written

$$\langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle = \sum_{i \neq 0} \langle \Phi_0 | \hat{S}^2 | \Psi_i \rangle \langle \Psi_i | \hat{S}^2 | \Phi_0 \rangle \Omega^{-2}. \quad (32)$$

With the following definition of the identity operator,

$$\hat{I} = \sum_{i \neq 0} |\Psi_i\rangle \langle \Psi_i| + |\Phi_0\rangle \langle \Phi_0| \quad \text{or} \quad (33)$$

$$\sum_{i \neq 0} |\Psi_i\rangle \langle \Psi_i| = \hat{I} - |\Phi_0\rangle \langle \Phi_0|,$$

Eq. (32) can be simplified

$$\begin{aligned} \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle &= \langle \langle \Phi_0 | \hat{S}^2 \hat{I} \hat{S}^2 | \Phi_0 \rangle \\ &\quad - \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle \rangle \Omega^{-2} \\ &= \langle \langle \Phi_0 | \hat{S}^4 | \Phi_0 \rangle - \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle \rangle \Omega^{-2}. \end{aligned} \quad (34)$$

In the notation of Amos and Synder,⁶ the expectation value of \hat{S}^4 is given as

$$\langle \Phi_0 | \hat{S}^4 | \Phi_0 \rangle = A_0(2) - A_1(2) \sum_{ij} \tilde{S}_{ij}^2 + 2 \left[\left(\sum_{ij} \tilde{S}_{ij}^2 \right)^2 - \sum_{ijkl} \tilde{S}_{ij} \tilde{S}_{kj} \tilde{S}_{kl} \tilde{S}_{il} \right], \quad (35)$$

where $A_0(2) = [s(s+1) + n_\beta]^2 + n_\alpha n_\beta$, $A_1(2) = 2[s(s+1) + n_\beta] + n_\alpha + n_\beta - 2$ and n_α , n_β are the number of alpha and beta electrons, respectively. The derivative of Eq. (33) can now be evaluated using Eqs. (11) and (35):

$$\begin{aligned} \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle^x &= (\langle \Phi_0 | \hat{S}^4 | \Phi_0 \rangle^x - 2 \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle^x \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle) \Omega^{-2} - 2 \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle^x \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle \Omega^{-1} \\ &= \left[-2A_1(2) \sum_{ij} \tilde{S}_{ij}^x \tilde{S}_{ij} + 8 \sum_{ij} \tilde{S}_{ij}^x \tilde{S}_{ij} \sum_{kl} \tilde{S}_{kl}^2 - 8 \sum_{ijkl} \tilde{S}_{ij}^x \tilde{S}_{kj} \tilde{S}_{kl} \tilde{S}_{il} \right] \Omega^{-2} \\ &\quad + 4 \sum_{ij} \tilde{S}_{ij}^x \tilde{S}_{ij} \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle \Omega^{-2} + 4 \sum_{ij} \tilde{S}_{ij}^x \tilde{S}_{ij} \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle \Omega^{-1} \\ &= \sum_{ij} \tilde{S}_{ij}^x W_{ij} \\ &= \sum_{ij} \tilde{S}_{ij}^{(X)} W_{ij} + \sum_{ijc} U_{ci} \tilde{S}_{cj} W_{ij} + \sum_{ijd} U_{dj} \tilde{S}_{id} W_{ij} - \frac{1}{2} \sum_{ijk} S_{ki}^{(X)} \tilde{S}_{kj} W_{ij} - \frac{1}{2} \sum_{ijl} S_{ij}^{(X)} \tilde{S}_{il} W_{ij}. \end{aligned} \quad (36)$$

This completes the derivation of all of the terms in Eq. (33) for the evaluation of the PMP2 gradients. In practice, the terms in Eqs. (21), (30), and (36) are combined with the corresponding terms in the MP2 gradient¹⁸ to yield the final coefficients of the U 's, $\tilde{S}^{(X)}$ and $\tilde{F}^{(X)}$.

This procedure can be interfaced with any program which provides a full solution of the CPHF equations,¹⁸ as in

the GAUSSIAN series of programs. Alternatively, the more efficient Z-vector method of Handy and Schaefer¹⁹ can be used (also available in GAUSSIAN 88¹⁵). In this case, all of the coefficients of the U 's in Eqs. (21), (30), and (36) must be added to the UMP2 Lagrangian before invoking the Z-vector reformulation. Both approaches for PMP2 gradients have been implemented in the development version of GAUS

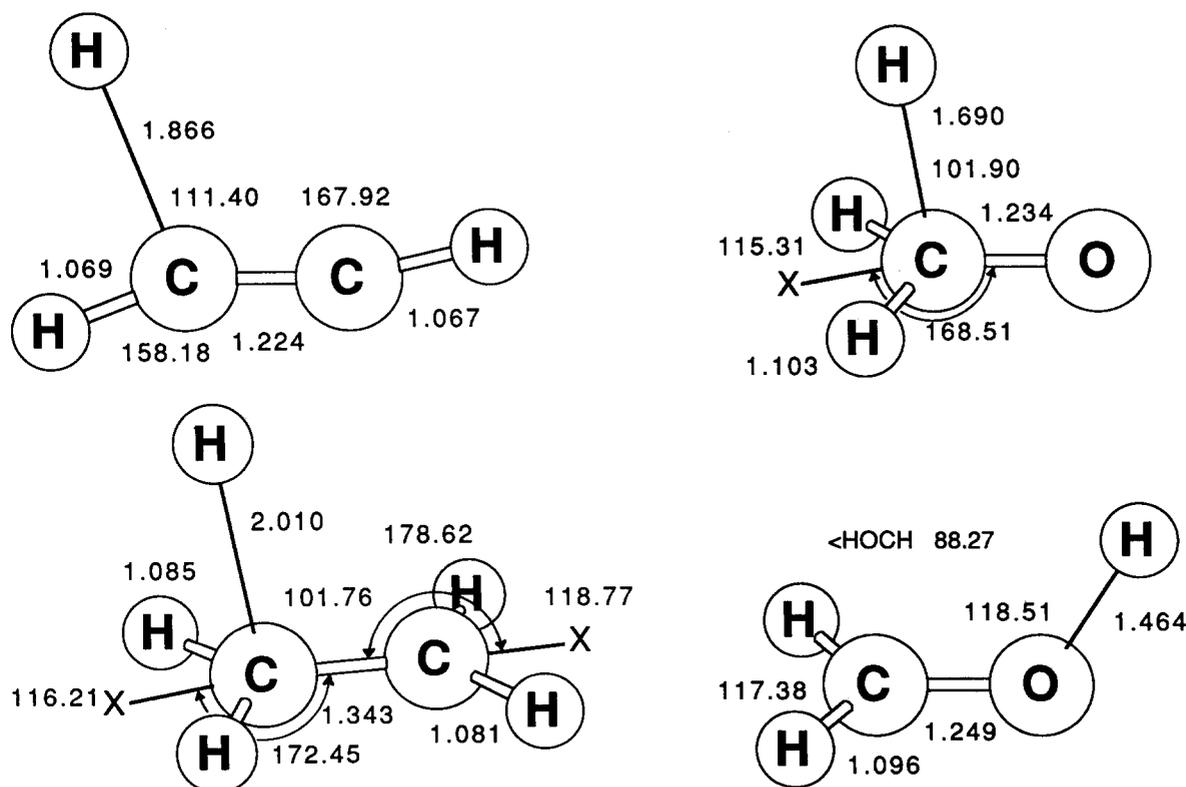


FIG. 1. Transition structure for (a) $\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3$, (b) $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$, (c) $\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}$, and (d) $\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH}$, optimized at the PMP2/6-31G* level with annihilation of the quartet spin contaminant.

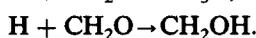
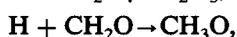
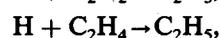
TABLE I. Total energies (E_n) of transition states and activation barriers (kcal/mol) for hydrogen addition reactions. Geometries optimized at the PMP2/6-31G* level.

	H--C ₂ H ₂	H--C ₂ H ₄	H--CH ₂ O	CH ₂ O--H
HF/6-31G*	-77.304 84	-78.524 61	-114.355 49	-114.338 36
MP2/6-31G*	-77.543 19	-78.764 73	-114.633 83	-114.622 25
PMP2/6-31G*	-77.559 46	-78.775 86	-114.648 73	-114.637 83
MP4/6-31G*	-77.577 27	-78.801 77	-114.665 52	-114.653 08
PMP4/6-31G*	-77.589 67	-78.810 50	-114.676 55	-114.664 80
HF/6-31G*	5.5	2.9	4.0	14.8
MP2/6-31G*	13.7	11.6	20.2	27.4
PMP2/6-31G*	3.5	4.6	10.8	17.6
MP4/6-31G*	9.1	10.2	15.5	23.3
PMP4/6-31G*	1.3	4.7	8.6	15.9

88. Relatively little additional computational work is required beyond that needed to evaluate unprojected UMP2 gradients.

APPLICATIONS

As an initial demonstration of the PMP2 gradient code, the following reactions involving the addition of hydrogen to multiple bonds have been reinvestigated^{11,13}:



Transition state geometries are shown in Fig. 1. Optimizations were carried out with the 6-31G* basis set²⁰ at the PMP2 level with annihilation of the quartet spin contaminant. The distance between the attacking hydrogen and the unsaturated species range from 0.006 Å longer (H + C₂H₄) to 0.14 Å shorter (H + CH₂O → CH₃O) than the UHF optimized geometries.^{11,13} Changes in the angle to the attacking hydrogen are -4.5° to 2.6°. The other coordinates are typically within 0.01 Å and 1° of the UHF values. Differences between the present optimization for H + C₂H₂ and a previous approximate grid search¹³ are primarily due to the use of single annihilation in the present work versus multiple annihilation in the previous study²¹ and, to a lesser extent, due to the numerical uncertainty in the grid search.

The computed barrier heights are collected in Table I. The energies were calculated with the 6-31G* basis set using the PMP2/6-31G* geometries given in Fig. 1 at the HF, MP2, MP4SDTQ, PMP2, and PMP4SDTQ levels with annihilation of all spin contaminants (not just the largest contaminant) and without zero point energy. For H + C₂H₄ and CH₂O, the present results are within 2 kcal/mol of the barrier heights computed previously at the UHF optimized geometry.¹¹ The results for H + C₂H₂ are ~5 kcal/mol lower than previous calculations with the same set; this may be a reflection of the sensitivity of position of the transition state to the degree of spin annihilation and the level of correlation corrections.^{13,23}

CONCLUSIONS

Spin contamination can cause significant problems in calculations using Møller–Plesset perturbation theory (MPn) based on single spin-unrestricted Hartree–Fock (UHF) reference determinants. Spin projection can overcome some of these difficulties, improving the shapes of energy surfaces and lowering barriers. Depending on the energy of the higher spin state, contamination of 1%–10% (e.g., $\langle \hat{S}^2 \rangle = (1-x^2)s(s+1) + x^2(s+1)(s+2)$, where x is the fraction of the next higher spin state contained in the UHF wave function) can result in errors of 1–10 kcal/mol. The effects of spin contamination on geometry are less predictable. Annihilation of the largest spin contaminant may be adequate if only one bond is broken (and/or one bond made) during a reaction; multiple annihilation is necessary if more than one bond is broken (e.g., symmetric stretch of H₂O). The development of gradients of MP2 energies with multiple spin annihilation is in progress.

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