

## IMPLEMENTATION OF ANALYTICAL ENERGY GRADIENTS AT THIRD- AND FOURTH-ORDER MØLLER-PLESSET PERTURBATION THEORY

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Formulas for the analytical gradients of the third- and fourth-order Møller–Plesset perturbation theory (MP3 and MP4(SDQ)) are given and their implementation discussed. The analytical gradients are applied to optimize the geometries of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> at the MP3/6-31G\* and MP4(SDQ)/6-31G\* levels. For H<sub>2</sub>O in addition, dipole moment, vibrational frequencies and infrared intensities are calculated

### 1. Introduction

Analytical derivatives of the energy have become a powerful tool in modern electronic structure calculations. They are widely used in exploring potential energy surfaces [1], determining equilibrium geometries [2], and calculating vibrational spectra [3]. At the HF, MC SCF and the CI level analytical gradients methods are routinely available [4]. However, gradient studies based on Møller–Plesset (MP) perturbation theory [5–8] have in general been restricted to the second-order level (MP2) [9]. In view of the fact that MP perturbation theory is one of the simplest methods of accounting for correlation effects in a systematic manner, the development and application of analytical gradients for third and fourth order (MP3 and MP4) is highly desirable.

Preliminary steps in this direction were made by Jørgensen and Simons [10] who derived an analytical expression for MP3 gradients. Recently, Fitzgerald and co-workers [11] reported on the successful implementation of analytical third-order many-body perturbation theory (MBPT3) gradients. Formulae for analytical MBPT4 gradients appeared in a publication by Fitzgerald, Harrison and Bartlett [12], after this work was completed.

While previous work on analytical gradients for third- and fourth-order perturbation theory was mainly based on MBPT and its coupled cluster extension [12], we will derive here expressions for MP3 and MP4 gradients by straightforward differentiation of the MP energy formulae, as given by Pople and co-workers [6–8]. In addition, we report on the implementation of third- and fourth-order MP gradients, neglecting only the contribution of the triples in the fourth-order expression [7]. This level, denoted MP4(SDQ), has been shown to yield a good compromise between the applicability of the method and accuracy of the results. Details concerning the implementation are discussed and the applicability of the developed programs are demonstrated by test calculations.

### 2. Theory

Let  $\Psi_0$  be the Hartree–Fock (HF) determinantal wavefunction with  $n$  occupied spin orbitals  $\phi_1, \dots, \phi_n$  which are eigenfunctions of the Fock operator  $\mathbf{F}$  with corresponding eigenvalues  $\epsilon_1, \dots, \epsilon_n$ . If the atomic orbital basis consists of  $N$  basis functions, there will be  $N-n$  unoccupied (virtual) orbitals  $\phi_{n+1}, \dots, \phi_N$ . In the following, labels  $i, j, k, l, m$  denote occupied spin orbitals, labels  $a, b, c, d, e$  virtual spin orbitals and labels  $p, q, r, s$  general orbitals.

In Møller–Plesset perturbation theory [5] the unperturbed Hamiltonian  $H_0$  is chosen as a sum of Fock operators:

$$H_0 = \sum_{\alpha} F(\alpha) \quad (1)$$

and the perturbed Hamiltonian  $H'$  is given as the difference between the electronic Hamiltonian  $H$  and  $H_0$ . With this choice the second-order perturbation correction to the energy is given by [5]

$$E(\text{MP2}) = \frac{1}{4} \sum_{ij} \sum_{ab} a(ij, ab) \langle ij || ab \rangle, \quad (2)$$

where  $a(ij, ab)$  denotes the first-order correction to the HF wavefunction:

$$a(ij, ab) = \langle ij || ab \rangle / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b), \quad (3)$$

and where the two-electron integral  $\langle pq || rs \rangle$  is defined by

$$\langle pq || rs \rangle = \iint \phi_p^*(1) \phi_q^*(2) |r_1 - r_2|^{-1} [\phi_r(1) \phi_s(2) - \phi_s(1) \phi_r(2)] d\tau_1 d\tau_2. \quad (4)$$

At third order the correlation correction is [6]

$$E(\text{MP3}) = \frac{1}{4} \sum_{ij} \sum_{ab} a(ij, ab) w(ij, ab) \quad (5)$$

with

$$w(ij, ab) = \frac{1}{2} \sum_{kl} \langle kl || ij \rangle a(kl, ab) + \frac{1}{2} \sum_{cd} \langle ab || cd \rangle a(ij, cd) \\ - \sum_k \sum_c [ \langle ka || ic \rangle a(kj, cb) + \langle ka || jc \rangle a(ik, cb) + \langle kb || ic \rangle a(kj, ac) + \langle kb || jc \rangle a(ik, ac) ]. \quad (6)$$

The fourth-order correction includes terms due to single, double, triple and quadruple excitations [7]. However, the contribution of the triples is the most expensive ( $\mathcal{O}(n^3 N^4)$  operations), so that the fourth-order correction is often approximated by considering only single, double and quadruple excitations [7] which requires only  $\mathcal{O}(n^3 N^3)$  operations. The corresponding energy expression is given by

$$E(\text{MP4}(\text{SDQ})) = \frac{1}{4} \sum_{ij} \sum_{ab} a(ij, ab) [v_S(ij, ab) + v_D(ij, ab) + v_Q(ij, ab)], \quad (7)$$

where  $v_S$ ,  $v_D$  and  $v_Q$  denote terms due to single, double, and quadruple excitations<sup>#1</sup>,

$$v_S(ij, ab) = \sum_c [ \langle ab || cj \rangle d(i, c) + \langle ab || ic \rangle d(j, c) ] - \sum_k [ \langle kb || ij \rangle d(k, a) + \langle ka || ji \rangle d(k, b) ], \quad (8)$$

$$v_D(ij, ab) = \frac{1}{2} \sum_{kl} \langle kl || ij \rangle d(kl, ab) + \frac{1}{2} \sum_{cd} \langle ab || cd \rangle d(ij, cd) \\ - \sum_k \sum_c [ \langle ka || ic \rangle d(kj, cb) + \langle ka || jc \rangle d(ik, cb) + \langle kb || ic \rangle d(kj, ac) + \langle kb || jc \rangle d(ik, ac) ] \quad (9)$$

and

$$v_Q(ij, ab) = \frac{1}{4} \sum_{kl} \sum_{cd} \langle kl || cd \rangle \{ a(ij, cd) a(kl, ab) - 2[a(ij, ac) a(kl, bd) + a(ij, bd) a(kl, ac)] \\ - 2[a(ik, ab) a(jl, cd) + a(ik, cd) a(jl, ab)] + 4[a(ik, ac) a(jl, bd) + a(ik, bd) a(jl, ac)] \} \quad (10)$$

<sup>#1</sup> The renormalization term is included here in the contribution of the quadruple excitations.

with

$$d(i, a) = w(i, a) / (\epsilon_i - \epsilon_a) \quad (11)$$

and

$$w(i, a) = \frac{1}{2} \sum_j \sum_b \left( \sum_c \langle aj \| cb \rangle a(ij, cb) - \sum_k \langle ib \| kj \rangle a(kj, ab) \right). \quad (12)$$

This approximate fourth-order expression possesses the same properties as the exact fourth-order term, i.e. size consistency and invariance under transformations amongst the occupied (virtual) orbitals [7].

Although the perturbed HF orbitals are not required for the evaluation of analytical MP $n$  gradients [13], it is convenient to use them in the derivation of the final formulae for the MP $n$  gradients. The coefficients of the perturbed orbitals  $c_{\mu p}^\lambda$  are usually expanded in terms of the unperturbed orbitals  $c_{\mu q}$  [9]:

$$c_{\mu p}^\lambda = \sum_q U_{qp}^\lambda c_{\mu q}. \quad (13)$$

The derivatives  $U_{pq}^\lambda$  are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations [9,14] for the HF wavefunction. They can be given in terms of the derivatives of the Fock matrix  $F_{qp}^\lambda$  and of the overlap matrix  $S_{qp}^\lambda$ ,

$$F_{qp}^\lambda = \sum_{\mu\nu} c_{\mu q} (\partial F_{\mu\nu} / \partial \lambda) c_{\nu p}, \quad (14a)$$

$$S_{qp}^\lambda = \sum_{\mu\nu} c_{\mu q} (\partial S_{\mu\nu} / \partial \lambda) c_{\nu p}. \quad (14b)$$

In the case of degeneracies  $U_{pq}^\lambda$  has a zero denominator and is no longer defined [9]. However, these terms can be eliminated from the corresponding gradient expressions by abandoning the requirement that the perturbed orbitals are canonical [15]. The derivatives  $U_{ij}^\lambda$  and  $U_{ab}^\lambda$  are then chosen in the simplest possible way [15] by

$$U_{ij}^\lambda = -\frac{1}{2} S_{ij}^\lambda \quad (15a)$$

and

$$U_{ab}^\lambda = -\frac{1}{2} S_{ab}^\lambda. \quad (15b)$$

Differentiation of the MP3 energy expression (5) with respect to  $\lambda$  yields

$$\begin{aligned} dE(\text{MP3})/d\lambda = & \frac{1}{2} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle^\lambda d(ij, ab) \\ & + \sum_{ij} \sum_{ab} a(ij, ab) \left( \frac{1}{2} \sum_{kl} \langle kl \| ij \rangle^\lambda a(kl, ab) + \frac{1}{2} \sum_{cd} \langle ab \| cd \rangle^\lambda a(ij, cd) - \sum_k \sum_c \langle ka \| ic \rangle^\lambda a(kj, cb) \right) \\ & - \sum_{ijm} \sum_{ab} a(mj, ab) \epsilon_{im}^\lambda d(ij, ab) + \sum_{ij} \sum_{abc} a(ij, cb) \epsilon_{ac}^\lambda d(ij, ab), \end{aligned} \quad (16)$$

where the derivatives of the two-electron integral  $\langle ij \| ab \rangle$  are given by [9]

$$\begin{aligned} \langle ij \| ab \rangle^\lambda = & \sum_{\mu\nu\sigma\rho} c_{\mu i} c_{\nu j} c_{\sigma a} c_{\rho b} \partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda \\ & + \sum_m (U_{ma}^\lambda \langle ij \| mb \rangle + U_{mb}^\lambda \langle ij \| am \rangle) + \sum_e (U_{ei}^\lambda \langle ej \| ab \rangle + U_{ej}^\lambda \langle ie \| ab \rangle) \\ & - \frac{1}{2} \sum_m (S_{mi}^\lambda \langle mj \| ab \rangle + S_{mj}^\lambda \langle im \| ab \rangle) - \frac{1}{2} \sum_e (S_{ea}^\lambda \langle ij \| eb \rangle + S_{eb}^\lambda \langle ij \| ae \rangle) \end{aligned} \quad (17)$$

and  $d(ij, ab)$  by

$$d(ij, ab) = w(ij, ab) / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) . \quad (18)$$

The derivatives of the Lagrangian multipliers  $\epsilon_{pq}^\lambda$  are

$$\begin{aligned} \epsilon_{pq}^\lambda = & h_{pq}^\lambda + \sum_{\mu\nu\sigma\rho} (\partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda) \sum_k c_{\mu p} c_{\nu k} c_{\sigma q} c_{\rho k} + \sum_a \sum_i U_{ai}^\lambda (\langle pa \| qi \rangle + \langle pi \| qa \rangle) \\ & - \frac{1}{2} \sum_y S_{ij}^\lambda (\langle pi \| qj \rangle + \langle pj \| qi \rangle) - \frac{1}{2} (\epsilon_p + \epsilon_q) S_{pq}^\lambda . \end{aligned} \quad (19)$$

By substituting eq. (17) into eq. (16) and reordering of the expression with respect to the different  $\lambda$ -dependent quantities, one obtains the formula

$$\begin{aligned} dE(\text{MP3})/d\lambda = & \sum_{\mu\nu\sigma\rho} (\partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda) T_{\mu\nu\sigma\rho}^{(3)} + \sum_a \sum_i U_{ai}^\lambda (L_{ai}'^{(3)} - L_{ia}''^{(3)}) \\ & - \frac{1}{2} \sum_{ij} S_{ij}^\lambda [L_{ij}'^{(3)} + (\epsilon_i + \epsilon_j) K_{ij}'^{(3)}] - \frac{1}{2} \sum_{ab} S_{ab}^\lambda [L_{ab}''^{(3)} + (\epsilon_a + \epsilon_b) K_{ab}''^{(3)}] \\ & - \sum_a \sum_i S_{ia}^\lambda L_{ia}''^{(3)} + \sum_{ij} h_{ij}^\lambda K_{ij}'^{(3)} + \sum_{ab} h_{ab}^\lambda K_{ab}''^{(3)} . \end{aligned} \quad (20)$$

The various terms in eq. (20) have the following meaning:

$$\begin{aligned} T_{\mu\nu\sigma\rho}^{(3)} = & \frac{1}{2} \sum_{ij} \sum_{ab} c_{\mu i} c_{\nu j} c_{\sigma a} c_{\rho b} d(ij, ab) \\ & + \frac{1}{2} \sum_{ij} \sum_{ab} a(ij, ab) \left( \sum_{cd} c_{\mu a} c_{\nu b} c_{\sigma c} c_{\rho d} a(ij, cd) + \sum_{kl} c_{\mu i} c_{\nu j} c_{\sigma k} c_{\rho l} a(kl, ab) - 8 \sum_k \sum_c c_{\mu k} c_{\nu a} c_{\sigma i} c_{\rho c} a(kj, cb) \right) \\ & + \sum_k c_{\nu k} c_{\rho k} \left( \sum_{ab} c_{\mu a} c_{\sigma b} K_{ab}''^{(3)} + \sum_{ij} c_{\mu i} c_{\sigma j} K_{ij}'^{(3)} \right) , \end{aligned} \quad (21a)$$

$$\begin{aligned} L_{pi}'^{(3)} = & \sum_j \sum_{ab} \langle pj \| ab \rangle d(ij, ab) + \frac{1}{2} \sum_j \sum_{ab} a(ij, ab) \left( \sum_{kl} \langle kl \| pj \rangle a(kl, ab) - 4 \sum_k \sum_c \langle ka \| pc \rangle a(kj, cb) \right) \\ & + \sum_{jk} K_{jk}'^{(3)} (\langle pj \| ik \rangle + \langle pk \| ij \rangle) + \sum_{ab} K_{ab}''^{(3)} (\langle pa \| ib \rangle + \langle pb \| ia \rangle) , \end{aligned} \quad (21b)$$

$$L_{pa}''^{(3)} = \sum_{ij} \sum_b \langle ij \| pb \rangle d(ij, ab) + \frac{1}{2} \sum_{ij} \sum_b a(ij, ab) \left( \sum_{cd} \langle pb \| cd \rangle a(ij, cd) - 4 \sum_k \sum_c \langle kp \| ic \rangle a(kj, cb) \right) , \quad (21c)$$

$$K_{ij}'^{(3)} = - \sum_k \sum_{ab} a(ik, ab) d(jk, ab) , \quad (21d)$$

$$K_{ab}''^{(3)} = \sum_{ij} \sum_c a(ij, ac) d(ij, bc) . \quad (21e)$$

An alternative formula for the MP3 gradient where all derivatives  $U_{ai}^\lambda$  have been eliminated is derived in the appendix.

An expression for the  $E(\text{MP4}(\text{SDQ}))$  gradient is obtained in an analogous way. Differentiation of (7) leads to

$$\begin{aligned}
 dE(\text{MP4}(\text{SDQ}))/d\lambda = & \frac{1}{2} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle^\lambda [e(ij, ab) + x(ij, ab)] \\
 & - \sum_{ijm} \sum_{ab} a(mj, ab) \epsilon_{im}^\lambda [e(ij, ab) + \frac{1}{2}x(ij, ab)] + \sum_{ij} \sum_{abc} a(ij, cb) \epsilon_{ac}^\lambda [e(ij, ab) + \frac{1}{2}x(ij, ab)] \\
 & + \sum_{ij} \sum_{ab} a(ij, ab) \left( \frac{1}{4} \sum_{kl} \langle kl \| ij \rangle^\lambda d(kl, ab) + \frac{1}{4} \sum_{cd} \langle ab \| cd \rangle^\lambda d(ij, cd) - 2 \sum_k \sum_c \langle ka \| ic \rangle^\lambda d(kj, cb) \right) \\
 & - \frac{1}{2} \sum_{ijm} \sum_{ab} d(mj, ab) \epsilon_{im}^\lambda d(ij, ab) + \frac{1}{2} \sum_{ij} \sum_{abc} d(ij, cb) \epsilon_{ac}^\lambda d(ij, ab) \\
 & + \sum_{ij} \sum_{ab} a(ij, ab) \left( \sum_c \langle ab \| cj \rangle^\lambda d(i, c) - \sum_k \langle kb \| ij \rangle^\lambda d(k, a) \right) \\
 & - \sum_{mi} \sum_a d(m, a) \epsilon_{im}^\lambda d(i, a) + \sum_i \sum_{ac} d(i, c) \epsilon_{ac}^\lambda d(i, a), \tag{22}
 \end{aligned}$$

with

$$e(ij, ab) = [v_S(ij, ab) + v_D(ij, ab) + v_Q(ij, ab)] / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \tag{23}$$

and #2

$$\begin{aligned}
 x(ij, ab) = & \frac{1}{4} \sum_{kl} \sum_{cd} a(kl, cd) \{ a(ij, cd) a(kl, ab) - 2[a(ij, ac) a(kl, bd) + a(ij, bd) a(kl, ac)] \\
 & - 2[a(ik, ab) a(jl, cd) + a(ik, cd) a(jl, ab)] + 4[a(ik, ac) a(jl, bd) + a(ik, bd) a(jl, ac)] \}. \tag{24}
 \end{aligned}$$

Substituting eq. (17) into the expression for the MP4(SDQ) gradient, eq. (22), and reordering leads to (for an alternative expression see the appendix)

$$\begin{aligned}
 dE(\text{MP4})/d\lambda = & \sum_{\mu\nu\sigma\rho} (\partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda) T_{\mu\nu\sigma\rho}^{(4)} + \sum_a \sum_i U_{ai}^\lambda (L'_{ai}{}^{(4)} - L''_{ia}{}^{(4)}) \\
 & - \frac{1}{2} \sum_{ij} S_{ij}^\lambda [L'_{ij}{}^{(4)} + (\epsilon_i + \epsilon_j) K'_{ij}{}^{(4)}] - \frac{1}{2} \sum_{ab} S_{ab}^\lambda [L''_{ab}{}^{(4)} + (\epsilon_a + \epsilon_b) K''_{ab}{}^{(4)}] \\
 & - \sum_a \sum_i S_{ia}^\lambda L''_{ia}{}^{(4)} + \sum_{ij} h_{ij}^\lambda K'_{ij}{}^{(4)} + \sum_{ab} h_{ab}^\lambda K''_{ab}{}^{(4)}, \tag{25}
 \end{aligned}$$

where the arrays  $T^{(4)}$ ,  $L'^{(4)}$ ,  $L''^{(4)}$ ,  $K'^{(4)}$ , and  $K''^{(4)}$  are defined according to

#2 The contribution of the quadruples to  $E(\text{MP4})$  is given alternatively by  $E(\text{MP4}(\text{Q})) = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle x(ij, ab)$ .

$$\begin{aligned}
T_{\mu\sigma\rho}^{(4)} = & \frac{1}{2} \sum_{ij} \sum_{ab} c_{\mu i} c_{\nu j} c_{\sigma a} c_{\rho b} [e(ij, ab) + x(ij, ab)] \\
& + \frac{1}{4} \sum_{ij} \sum_{ab} a(ij, ab) \left( \sum_{cd} c_{\mu a} c_{\nu b} c_{\sigma c} c_{\rho d} d(ij, cd) + \sum_{kl} c_{\mu i} c_{\nu j} c_{\sigma k} c_{\rho l} d(kl, ab) - 8 \sum_k \sum_c c_{\mu k} c_{\nu a} c_{\sigma i} c_{\rho c} d(kj, cb) \right) \\
& + \sum_{ij} \sum_{abc} c_{\mu a} c_{\nu b} c_{\sigma c} c_{\rho j} a(ij, ab) d(i, c) - \sum_{ijk} \sum_{ab} c_{\mu k} c_{\nu b} c_{\sigma i} c_{\rho j} a(ij, ab) d(k, a) \\
& + \sum_k c_{\nu k} c_{\rho k} \left( \sum_{ab} c_{\mu a} c_{\sigma b} K_{ab}''^{(4)} + \sum_{ij} c_{\mu i} c_{\sigma j} K_{ij}'^{(4)} \right), \tag{26a}
\end{aligned}$$

$$\begin{aligned}
L_{pi}'^{(4)} = & \sum_j \sum_{ab} \langle pj \| ab \rangle [e(ij, ab) + x(ij, ab)] \\
& + \frac{1}{2} \sum_j \sum_{ab} a(ij, ab) \left( \sum_{kl} \langle kl \| pj \rangle d(kl, ab) - 4 \sum_k \sum_c \langle ka \| pc \rangle d(kj, cb) \right) \\
& + \frac{1}{2} \sum_j \sum_{ab} d(ij, ab) \left( \sum_{kl} \langle kl \| pj \rangle a(kl, ab) - 4 \sum_k \sum_c \langle ka \| pc \rangle a(kj, cb) \right) \\
& - 2 \sum_{jk} \sum_{ab} a(ij, ab) \langle kb \| pj \rangle d(k, a) - \sum_{jk} \sum_{ab} a(jk, ab) \langle jk \| pb \rangle d(i, a) \\
& + \sum_j \sum_{abc} a(ij, ab) \langle ab \| pc \rangle d(j, c) + \sum_{jk} K_{jk}''^{(4)} (\langle pj \| ik \rangle + \langle pk \| ij \rangle) \\
& + \sum_{ab} K_{ab}''^{(4)} (\langle pa \| ib \rangle + \langle pb \| ia \rangle), \tag{26b}
\end{aligned}$$

$$\begin{aligned}
L_{pa}''^{(4)} = & \sum_{ij} \sum_b \langle ij \| pb \rangle [e(ij, ab) + x(ij, ab)] \\
& + \frac{1}{2} \sum_{ij} \sum_b a(ij, ab) \left( \sum_{cd} \langle pb \| cd \rangle d(ij, cd) - 4 \sum_k \sum_c \langle kp \| ic \rangle d(kj, cb) \right) \\
& + \frac{1}{2} \sum_{ij} \sum_b d(ij, ab) \left( \sum_{cd} \langle pb \| cd \rangle a(ij, cd) - 4 \sum_k \sum_c \langle kp \| ic \rangle a(kj, cb) \right) \\
& + 2 \sum_{ij} \sum_{bc} a(ij, ab) \langle pb \| cj \rangle d(i, c) + \sum_{ij} \sum_{bc} a(ij, bc) \langle bc \| pj \rangle d(i, a) - \sum_{ijk} \sum_b a(ij, ab) \langle kp \| ji \rangle d(k, b), \tag{26c}
\end{aligned}$$

$$K_y'^{(4)} = - \sum_k \sum_{ab} a(ik, ab) [e(jk, ab) + \frac{1}{2} x(jk, ab)] - \frac{1}{2} \sum_k \sum_{ab} d(ik, ab) d(jk, ab) - \sum_a d(i, a) d(j, a), \tag{26d}$$

$$K_{ab}''^{(4)} = \sum_{ij} \sum_c a(ij, ac) [e(ij, bc) + \frac{1}{2} x(ij, bc)] + \frac{1}{2} \sum_{ij} \sum_c d(ij, ac) d(ij, bc) + \sum_i d(i, a) d(i, b). \tag{26e}$$

It should be noted that at each order of MP perturbation theory the gradient expression can be written in the following form:

$$\begin{aligned} dE(\text{MP}n)/d\lambda = & \sum_{\mu\nu\sigma\rho} (\partial\langle\mu\nu\|\sigma\rho\rangle/\partial\lambda) T_{\mu\nu\sigma\rho}^{(n)} + \sum_a \sum_i U_{ai}^\lambda (L_{ai}'^{(n)} - L_{ia}''^{(n)}) \\ & - \frac{1}{2} \sum_{ij} S_{ij}^\lambda [L_{ij}'^{(n)} + (\epsilon_i + \epsilon_j) K_{ij}'^{(n)}] - \frac{1}{2} \sum_{ab} S_{ab}^\lambda [L_{ab}''^{(n)} + (\epsilon_a + \epsilon_b) K_{ab}''^{(n)}] \\ & - \sum_a \sum_i S_{ia}^\lambda L_{ia}''^{(n)} + \sum_{ij} h_{ij}^\lambda K_{ij}'^{(n)} + \sum_{ab} h_{ab}^\lambda K_{ab}''^{(n)}, \end{aligned} \quad (27)$$

where the factors  $T^{(n)}$ ,  $L'^{(n)}$ ,  $L''^{(n)}$ ,  $K'^{(n)}$ , and  $K''^{(n)}$  are independent of the perturbation parameter  $\lambda$ . All the derivatives  $U_{ai}^\lambda$  can be eliminated from the MP $n$  gradient expression (27) as is shown in the appendix.

### 3. Implementation

For a MP4(SDQ) calculation, the arrays  $a(ij, ab)$ ,  $w(ij, ab)$ ,  $v_Q(ij, ab)$  and  $w(i, a)$  are required for determining the molecular energy. In addition, for a gradient calculation the arrays  $v_S(ij, ab)$ ,  $v_D(ij, ab)$  and  $x(ij, ab)$  have to be evaluated. Using these arrays and the transformed two-electron integrals  $\langle pq\|rs\rangle$ , the factors  $L'_{pq}$ ,  $L''_{pq}$ ,  $K'_{pq}$  and  $K''_{pq}$  in eqs. (20) and (25) are computed and stored. The current implementation of the MP3 and MP4(SDQ) gradient requires the solution of the CPHF equations. This, however, is a relatively inexpensive step compared to other parts of the MP3 and MP4(SDQ) gradient calculation.

The evaluation of the term  $T_{\mu\nu\sigma\rho}$  requires a four-index transformation from the MO basis to the AO basis. In order to avoid the storage of the two-electron integral derivatives the corresponding contribution to the MP $n$  gradient is formed immediately after the integral derivative  $\partial\langle\mu\nu\|\sigma\rho\rangle/\partial\lambda$  has been calculated [16]. A sort of the  $T_{\mu\nu\sigma\rho}$  elements according to the different shell combinations prior to the integral derivative calculation is required in this case. In order to avoid redundant operations all contributions to the energy gradient from the different orders MP perturbation theory are evaluated simultaneously.

Programs for evaluating the MP3 and MP4(SDQ) gradients based on the final formulae (20), (21), (25) and (26) have been written and implemented in the program system COLOGNE [17]<sup>\*3</sup>. Careful checking of the programs has been carried out by comparisons with numerically evaluated energy gradients.

### 4. Applications

To illustrate the applicability of the implemented computer programs, we calculated for H<sub>2</sub>O the equilibrium geometry, the dipole moment, harmonic vibrational frequencies, and infrared intensities at the MP3 and MP4(SDQ) levels using analytically evaluated gradients and the 6-31G\* basis [19]. The dipole moment is determined as the derivative of the energy with respect to a static electric field. Force constants and dipole moment derivatives were evaluated by numerical differentiation. The results obtained are summarized in table 1 along with the corresponding results at the HF and MP2 level [20-22].

In addition, we optimized the geometry of H<sub>2</sub>O<sub>2</sub> at the MP3/6-31G\*, MP4(SDQ)/6-31G\* and MP4(SDQ)/6-311 + G\*\* level, respectively. The geometrical parameters are listed in table 2 together with the corresponding HF and MP2 results [28] and the experimentally determined geometry. Clearly, the HF method fails to reproduce the correct equilibrium geometry, in particular the OO bond length is too short by 0.06 Å. Inspection of table 2 reveals that the main effect of electron correlation on the equilibrium geometry is covered by the MP2

<sup>\*3</sup> COLOGNE is a program system developed for a CDC Cyber 176 computer and contains large parts of GAUSSIAN 82 [18].

Table 1

Theoretical energies, geometries, dipole moments, harmonic vibrational frequencies, and infrared intensities of H<sub>2</sub>O<sup>a)</sup>

	HF/6-31G* <sup>b)</sup>	MP2/6-31G* <sup>c)</sup>	MP3/6-31G*	MP4(SDQ)/ 6-31G*	Exp. <sup>d)</sup>
$r_{\text{OH}}$	0.9473	0.9685	0.9666	0.9686	0.957
$\alpha_{\text{HOH}}$	105.50	104.05	104.24	104.11	104.5
$E$	-76.01075	-76.19924	-76.20488	-76.20766	-
$\mu$	2.199	2.199	2.188	2.179	1.85
$\nu_1$	4189	3919	3930	3893	3756(3942)
$\nu_2$	4071	3778	3809	3765	3657(3832)
$\nu_3$	1827	1734	1750	1745	1595(1648)
$I_1$	58.1	39.2	31.1	26.2	44.6
$I_2$	18.2	5.6	4.9	3.3	2.2
$I_3$	107.3	88.9	89.8	86.3	53.6

<sup>a)</sup> Energies in hartree, distances in Å, angles in deg, dipole moment  $\mu$  in D, vibrational frequencies  $\nu$  in cm<sup>-1</sup>, intensities  $I$  in km/mol.<sup>b)</sup> See ref. [20].<sup>c)</sup> Geometry from ref. [21] and vibrational frequencies from ref. [22].<sup>d)</sup>  $r_e$ -geometry from ref. [23], dipole moment from ref. [24], vibrational frequencies from ref. [25], and intensities from ref. [26]. Experimentally derived harmonic frequencies are given in parentheses [27].

Table 2

Theoretical geometries and energies of hydrogen peroxide, H<sub>2</sub>O<sub>2</sub><sup>a)</sup>

	HF/6-31G* <sup>b)</sup>	MP2/6-31G* <sup>b)</sup>	MP3/6-31G*	MP4(SDQ)/ 6-31G*	MP4(SDQ)/ 6-311++G**	Exp. <sup>b)</sup>
$r_{\text{OO}}$	1.3965	1.4681	1.4524	1.4640	1.4433	1.452
$r_{\text{OH}}$	0.9492	0.9756	0.9714	0.9744	0.9620	0.965
$\alpha_{\text{HOO}}$	102.08	98.66	99.69	99.29	100.23	100.1
$\tau_{\text{HOOH}}$	116.00	121.19	121.11	120.86	119.31	119.1
$E$	-150.76479	-151.13492	-151.14032	-151.14689	-151.29124	-

<sup>a)</sup> Energies in hartree, distances in Å, and angles in deg. <sup>b)</sup> See ref. [28]

correction. The MP2/6-31G\* geometry is in reasonable accord with the experimental geometry. Deviations are mainly due to the basis set. The use of a larger [4s3p1d/2s1p] basis improves the agreement considerably [28]. Inclusion of third-order corrections shortens the OO bond length which means that an improvement of the basis at the MP3 level will lead to a OO bond length about 0.01–0.02 Å too short. The MP4(SDQ) geometry on the other hand is very similar to the MP2 geometry. As expected from the MP2 results, optimization at the MP4(SDQ) level with a larger basis leads to a geometry very close to the  $r_e$  geometry (table 2).

Compared to numerical gradients, analytical gradients are more accurate and faster to evaluate. For example, the calculation of the MP4(SDQ)/6-311++G\*\* gradient for H<sub>2</sub>O<sub>2</sub> took on a Cray X-MP/24 about 2.1 times as long as a single MP4(SDQ) energy calculation.

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## Appendix

Following Handy and Schaefer [13] the derivatives  $U_{ai}^\lambda$  can be eliminated from the MP $n$  gradient expression (27). The CPHF equations take the form [9,14]

$$\sum_a \sum_i (A_{bjai} + \epsilon_a \delta_{ab} - \epsilon_i \delta_{ij}) U_{ai}^\lambda = B_{bj}^\lambda, \quad (\text{A1})$$

where  $B_{bj}^\lambda$  is completely defined by the derivatives of the one- and two-electron integrals

$$B_{bj}^\lambda = -h_{bj}^\lambda - \sum_{\mu\nu\sigma\rho} (\partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda) \sum_k c_{\mu b} c_{\nu k} c_{\sigma j} c_{\rho k} + \frac{1}{2} \sum_{kl} A_{klbj} S_{kl}^\lambda + \epsilon_j S_{bj}^\lambda \quad (\text{A2})$$

and  $A_{pqrs}$  is independent of the perturbation  $\lambda$

$$A_{pqrs} = \langle pr \| qs \rangle + \langle ps \| qr \rangle. \quad (\text{A3})$$

Defining  $Z_{bj}^{(n)}$  by the equation

$$\sum_b \sum_j (A_{bjai} + \epsilon_a \delta_{ab} - \epsilon_i \delta_{ij}) Z_{bj}^{(n)} = L_{ai}'^{(n)} - L_{ia}''^{(n)} \quad (\text{A4})$$

the second term in eq. (27) which contains  $U_{ai}^\lambda$  can be replaced:

$$\sum_a \sum_i (L_{ai}'^{(n)} - L_{ia}''^{(n)}) U_{ai}^\lambda = \sum_b \sum_j B_{bj}^\lambda Z_{bj}^{(n)}. \quad (\text{A5})$$

Instead of solving  $M$  sets of linear equations (eqs. (A1)), where  $M$  is the number of perturbation parameters, only one set of equations (eqs. (A4)), has to be solved. The final expression for the MP $n$  gradient is then rewritten in the form

$$dE(\text{MP}n)/d\lambda = \sum_{\mu\nu\sigma\rho} (\partial \langle \mu\nu \| \sigma\rho \rangle / \partial \lambda) G_{\mu\nu\sigma\rho}^{(n)} + \sum_{\mu\nu} h_{\mu\nu}^\lambda D_{\mu\nu}^{(n)} + \sum_{\mu\nu} S_{\mu\nu}^\lambda C_{\mu\nu}^{(n)}, \quad (\text{A6})$$

where the matrices  $G_{\mu\nu\sigma\rho}^{(n)}$ ,  $D_{\mu\nu}^{(n)}$ , and  $C_{\mu\nu}^{(n)}$  are defined by

$$G_{\mu\nu\sigma\rho}^{(n)} = T_{\mu\nu\sigma\rho}^{(n)} - \sum_{ij} \sum_a Z_{ai}^{(n)} c_{\mu a} c_{\sigma i} c_{\nu j} c_{\rho j}, \quad (\text{A7a})$$

$$D_{\mu\nu}^{(n)} = \sum_{ij} c_{\mu i} c_{\nu j} K_{ij}'^{(n)} + \sum_{ab} c_{\mu a} c_{\nu b} K_{ab}''^{(n)} - \sum_a \sum_i c_{\mu a} c_{\nu i} Z_{ai}^{(n)}, \quad (\text{A7b})$$

$$C_{\mu\nu}^{(n)} = -\frac{1}{2} \sum_{ij} c_{\mu i} c_{\nu j} \left( L_{ij}'^{(n)} - \sum_a \sum_k A_{akij} Z_{ak}^{(n)} + (\epsilon_i + \epsilon_j) K_{ij}'^{(n)} \right) \\ - \frac{1}{2} \sum_{ab} c_{\mu a} c_{\nu b} [ L_{ab}''^{(n)} + (\epsilon_a + \epsilon_b) K_{ab}''^{(n)} ] - \sum_a \sum_i c_{\mu a} c_{\nu i} ( L_{ia}''^{(n)} - \epsilon_i Z_{ai}^{(n)} ). \quad (\text{A7c})$$

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