ANALYTICAL DIFFERENTIATION OF THE ENERGY CONTRIBUTION
DUE TO TRIPLE EXCITATIONS
IN QUADRATIC CONFIGURATION INTERACTION THEORY

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Formulae for the analytical differentiation of the energy contribution due to triple excitations (T) within quadratic configuration interaction (QCI) theory are derived. Combining these formulae with previously derived formulae for the evaluation of analytical first derivatives for QCI theory with single (S) and double excitations (D), an algorithm is developed to calculate analytical QCISD(T) energy gradients. The applicability of this algorithm is demonstrated by calculating the equilibrium geometry of CH_2OO at the QCISD(T)/6-31G(d, p) level of theory.

1. Introduction

Pople, Head-Gordon and Raghavachari introduced a new method for the calculation of the electron correlation energy starting from the single determinant approach of Hartree–Fock (HF) theory [1]. The authors called this method quadratic configuration interaction (QCI) since they derived it from normal configuration interaction theory by adding new terms which are quadratic in the configuration coefficients. The quadratic terms ensure size-consistency in the total molecular energy [1]. When only single (S) and double (D) excitations are included in the QCI approach (QCISD), it is closely related to coupled cluster (CC) theory at the CCSD level [2]. Pople and co-workers have stressed the simplicity of QCISD as compared to CCSD and have considered QCISD as an intermediate approach between CC and CI theory. The relationship between QCISD and CCSD has been analyzed by Paldus, Čížek and Jeziorski [3] and the computational requirements of the two methods by Scuseria and Schaefer [4].

In their original paper, Pople and co-workers also introduced a useful approximation for handling triple excitations (T) at the QCI level of theory [1]. They treat the triple excitations as a small perturbation of the solution obtained at the QCISD level. Perturbation theory yields for the energy correction due to the triples the term $\Delta E(T)$ (see below) which is simply added to the QCISD energy to yield a QCISD(T) energy. Comparison of QCISD(T) results with those of full CI and other methods have led to promising results in a number of cases [1].

We have presented analytical formulae for the energy gradient within QCISD theory [5]. We have also developed expressions for the analytical gradient of the energy contribution due to triple excitations within fourth-order Møller–Plesset (MP4) perturbation theory [6]. We have implemented these formulae in a computer program and have discussed the advantage of using analytical gradients for QCISD and MP4(SDTQ) theory [5,6]. In this work we extend our previous results by presenting the theory for the analytical differentiation of the triple correction $\Delta E(T)$ within QCISD(T) theory introduced by Pople and co-workers [1].

2. Theory

The energy correction due to triple excitations in QCISD(T) theory is given by

$$\Delta E(\mathrm{T}) = \tfrac{1}{36} \sum_{ijk} \sum_{abc} d(ijk, abc) \, [w(ijk, abc) + 2\tilde{w}(ijk, abc)] . \tag{1}$$

The matrix elements in eq. (1) are defined as

$$w(ijk, abc) = \sum_{d} [a_{ij}^{ad} \langle bc \| dk \rangle + a_{ij}^{bd} \langle ca \| dk \rangle + a_{ij}^{cd} \langle ab \| dk \rangle + a_{ki}^{ad} \langle bc \| dj \rangle + a_{ki}^{bd} \langle ca \| dj \rangle$$

$$+ a_{ki}^{cd} \langle ab \| dj \rangle + a_{jk}^{ad} \langle bc \| di \rangle + a_{jk}^{bd} \langle ca \| di \rangle + a_{jk}^{cd} \langle ab \| di \rangle]$$

$$+ \sum_{m} [a_{im}^{ab} \langle cm \| jk \rangle + a_{im}^{bc} \langle am \| jk \rangle + a_{im}^{ca} \langle bm \| jk \rangle + a_{jm}^{ab} \langle cm \| ki \rangle + a_{jm}^{bc} \langle am \| ki \rangle$$

$$+ a_{jm}^{ca} \langle bm | ki \rangle + a_{km}^{ab} \langle cm \| ij \rangle + a_{km}^{bc} \langle am \| ij \rangle + a_{km}^{ca} \langle bm \| ij \rangle] , \tag{2}$$

$$d(ijk, abc) = w(ijk, abc) / (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c) , \tag{3}$$

$$\tilde{w}(ijk, abc) = a_i^a \langle jk \| bc \rangle + a_i^b \langle jk \| ca \rangle + a_i^c \langle jk \| ab \rangle + a_j^a \langle ki \| bc \rangle + a_j^b \langle ki \| ca \rangle$$

$$+ a_j^c \langle ki \| ab \rangle + a_k^a \langle ij \| bc \rangle + a_k^b \langle ij \| ca \rangle + a_k^c \langle ij \| ab \rangle , \tag{4}$$

$$\tilde{d}(ijk, abc) = \tilde{w}(ijk, abc) / (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c) . \tag{5}$$

In eqs. (2) to (5), the symbols a_i^a and a_{ij}^{ab} represent the converged QCISD amplitudes of single and double excitations, respectively. The double-bar integrals $\langle pq \| rs \rangle$ correspond to antisymmetrized two-electron integrals in the spin-orbital representation:

$$\langle pq \| rs \rangle = \int \varphi_p^*(1) \, \varphi_q^*(2) \, |r_1 - r_2|^{-1} [\varphi_r(1) \, \varphi_s(2) - \varphi_s(1) \, \varphi_r(2)] \, d\tau_1 \, d\tau_2 , \tag{6}$$

with φ_p being a HF spin orbital and ϵ_p being the corresponding orbital energy. The labels $i, j, k, \ldots$ denote occupied orbitals, labels $a, b, c, \ldots$ virtual orbitals and labels $p, q, r, \ldots$ any orbital either occupied or not.

Differentiation of eq. (1) with respect to an external perturbation parameter λ, e.g. the displacement of a nuclear coordinate or the component of a static electric field, leads to the following expression for the gradient of the energy correction $\Delta E(\mathrm{T})$ in QCISD(T) theory:

$$d[\Delta E(\mathrm{T})] / d\lambda = \tfrac{1}{36} \sum_{ijk} \sum_{abc} w(ijk, abc)^\lambda [2d(ijk, abc) + 2\tilde{d}(ijk, abc)] + \tfrac{1}{36} \sum_{ijk} \sum_{abc} \tilde{w}(ijk, abc)^\lambda \, 2d(ijk, abc)$$

$$- \tfrac{1}{12} \sum_{ijkl} \sum_{abc} \epsilon_{kl}^\lambda d(ijk, abc) [d(ijl, abc) + 2\tilde{d}(ijl, abc)] + \tfrac{1}{12} \sum_{ijk} \sum_{abcd} \epsilon_{cd}^\lambda d(ijk, abc) [d(ijk, abd) + 2\tilde{d}(ijk, abd)] , \tag{7}$$

with $w(ijk, abc)^\lambda$, ϵ_{kl}^λ, etc. being the derivative of the elements of w, ϵ, etc. with respect to λ.

In order to avoid singularities in the evaluation of eq. (7) the derivatives of the Lagrangian multipliers ϵ_{pq} rather than those of the canonical orbital energies are calculated [7]. Substitution of eqs. (2) and (4) into eq. (7) leads to

$$d[\Delta E(\mathrm{T})] / d\lambda = \tfrac{1}{2} \sum_{ij} \sum_{ab} [a_{ij}^{ab}]^\lambda v_\mathrm{T}(ij, ab) + 2 \sum_{ijk} \sum_{a} \langle ij \| ka \rangle^\lambda r(ijk, a) + 2 \sum_{i} \sum_{abc} \langle ia \| bc \rangle^\lambda s(i, abc)$$

$$+ \sum_{i} \sum_{a} [a_i^a]^\lambda v_\mathrm{T}(i, a) + \tfrac{1}{2} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle^\lambda u(ij, ab) + \sum_{ab} \epsilon_{ab}^\lambda t(a, b) - \sum_{ij} \epsilon_{ij}^\lambda t(i, j) , \tag{8}$$

where $[a_i^a]^\lambda$ and $[a_{ij}^{ab}]^\lambda$ denote the derivatives of the amplitudes a_i^a and a_{ij}^{ab} with respect to λ.

The matrices v_T, r, s, t, and u are defined in the following way:

$$v_{\rm T}(ij, ab) = \tfrac{1}{2} \sum_k \sum_{cd} [\langle cd\|bk\rangle\{d(ijk, acd) + \tilde{d}(ijk, acd)\} - \langle cd\|ak\rangle\{d(ijk, bcd) + \tilde{d}(ijk, bcd)\}] \tag{9}$$

$$+ \tfrac{1}{2} \sum_{kl} \sum_c [\langle cj\|kl\rangle\{d(ikl, abc) + \tilde{d}(ikl, abc)\} - \langle ci\|kl\rangle\{d(jkl, abc) + \tilde{d}(jkl, abc)\}] \,,$$

$$r(ijk, a) = \tfrac{1}{4} \sum_l \sum_{bc} a_{kl}^{bc}\{d(ijl, abc) + \tilde{d}(ijl, abc)\} \,, \tag{10}$$

$$s(i, abc) = \tfrac{1}{4} \sum_{jk} \sum_d a_{jk}^{ad}\{d(ijk, bcd) + \tilde{d}(ijk, bcd)\} \,, \tag{11}$$

$$t(p, q) = \tfrac{1}{12} \sum_{kl} \sum_{abc} d(ikl, abc)\{d(jkl, abc) + \tilde{d}(jkl, abc)\}, \quad \text{for } p=i \text{ and } q=j \,, \tag{12a}$$

$$= \tfrac{1}{12} \sum_{ijk} \sum_{cd} d(ijk, acd)\{d(ijk, bcd) + \tilde{d}(ijk, bcd)\}, \quad \text{for } p=a \text{ and } q=b \,, \tag{12b}$$

$$u(ij, ab) = \sum_k \sum_c d(ijk, abc)\, a_k^c \,, \tag{13}$$

$$v_T(i, a) = \tfrac{1}{2} \sum_{jk} \sum_{bc} d(ijk, abc)\langle jk\|bc\rangle \,. \tag{14}$$

The formula for the first derivative of $\Delta E({\rm T})$ with respect to an external perturbation λ is very similar to the previously derived expression for the analytical gradient of the corresponding energy correction within fourth-order Møller–Plesset (MP4) perturbation theory [6]. Differences in the two formulae are due to (a) the different definitions of the amplitudes a_{ij}^{ab} and a_i^q in QCI and MP theory and (b) the additional coupling of single and triple excitations present in QCI theory but absent in MP4 theory. This coupling leads to terms involving $v_{\rm T}(i, a)$ and $u(ij, ab)$ in eq. (8) as well as to the terms $d(ijk, abc)$ in eqs. (9) to (12).

As has already been stressed in connection with the evaluation of the QCISD gradients [5], explicit calculation of the derivatives of the amplitudes a_i^q and a_{ij}^{ab} is very time consuming and should be eliminated utilizing the z-vector method of Handy and Schaefer [8]. While the coupled perturbed QCI equations that are required to determine the derivatives of a_i^q and a_{ij}^{ab}, in eq. (8) are identical in QCISD and QCISD(T) theory, the corresponding z-vector equations are not. Here, additional terms resulting from the derivatives of a_i^q and a_{ij}^{ab} have to be added to the inhomogeneous terms. Within QCISD(T) theory the z-vector equations are given by

$$\sum_j \sum_b z_j^b C_{j,i}^{b,a} + \sum_{j<k} \sum_{b<c} z_{jk}^{bc} C_{jk,i}^{bc,a} = v_{\rm T}(i, a) \,, \tag{15a}$$

$$\sum_k \sum_c z_k^c C_{k,ij}^{c,ab} + \sum_{k<l} \sum_{c<d} z_{kl}^{cd} C_{kl,ij}^{cd,ab} = \langle ab\|ij\rangle + 2v_{\rm T}(ij, ab) \,. \tag{15b}$$

For a definition of the various C terms in eq. (15) and a full account of the use of the z-vector method in QCI gradient theory compare with ref. [5].

The contribution of triple excitations to the QCISD(T) gradient comprises two terms, one which is included already in the QCISD energy gradient (after modifying the z-vector equations as described above) and one which is given by additional terms containing derivatives of the two-electron integrals and the orbital energies:

$$dE[{\rm QCISD(T)}]/d\lambda = dE[{\rm QCISD}]/d\lambda + 2 \sum_{ijk} \sum_a \langle ij\|ka\rangle^\lambda r(ijk, a) + 2 \sum_i \sum_{abc} \langle ia\|bc\rangle^\lambda s(i, abc)$$

$$+ \tfrac{1}{2} \sum_{ij} \sum_{ab} \langle ij\|ab\rangle^\lambda u(ij, ab) + \sum_{ab} \epsilon_{ab}^\lambda t(a, b) - \sum_{ij} \epsilon_{ij}^\lambda t(i, j) \,. \tag{16}$$

Eq. (16) can be rearranged into a form containing only AO integral derivatives, namely the derivatives of the two-electron integrals $\langle \mu\nu\|\sigma\rho\rangle$, of the one-electron integrals $h_{\mu\nu}$, and of the overlap integrals $S_{\mu\nu}$. In addition, one needs the derivatives U_{ai}^λ of the spin-orbital coefficients $c_{\mu\rho}$ as they are defined in the usual coupled-

perturbed HF (CPHF) theory [9,10]. The solution of the CPHF equations is avoided by again using the z-vector method [8]. The QCISD(T) energy gradient can be written as

$$dE[QCISD(T)]/d\lambda = \sum_{\mu\nu\sigma\rho} T_{\mu\nu\sigma\rho} \langle \mu\nu\|\sigma\rho\rangle^\lambda + \sum_{\mu\nu} D_{\mu\nu} h^\lambda_{\mu\nu} + \sum_{\mu\nu} C_{\mu\nu} S^\lambda_{\mu\nu}, \tag{17}$$

where $T_{\mu\nu\sigma\rho}$, $D_{\mu\nu}$, $C_{\mu\nu}$ are independent of the perturbation λ but dependent on the solution of the z-vector equations.

3. Implementation

Computer programs for the analytical evaluation of the energy correction due to triple excitations in QCI theory have been written and combined with the existing programs for the evaluation of the analytical QCISD gradient [5] contained in the program system COLOGNE [11]. Since the evaluation of the various terms of the QCISD(T) gradient is similar to those needed for MP4(T) gradients [6] the implementation follows the same procedure described in our paper on the calculation of the analytical energy gradient for MP4(SDTQ) [6]. In this procedure, storage of the arrays $d(ijk, abc)$ and $\tilde{d}(ijk, abc)$ is avoided by using a direct algorithm for the computation of $v_T(ij, ab)$, $v_T(i, a)$, $r(ijk, a)$, $s(i, abc)$, $t(p, q)$ and $u(ij, ab)$. This means that the appropriate contributions of the triple amplitudes to these arrays is immediately evaluated when the corresponding triple amplitudes have been determined.

The solution of the z-vector equations within coupled-perturbed QCI theory as well as the evaluation of the terms for the QCISD gradients has been described in ref. [5]. This procedure has been modified to incorporate the additional inhomogeneous terms in the z-vector equations. The programs for the analytical evaluation of the QCISD(T) gradients have been carefully checked by comparing results with those obtained by numerical differentiation. Calculation of the analytical QCISD(T) gradient turns out to require 3–4 times the costs of a QCISD(T) single-point calculation. This has also been found in the case of the analytical MP4(SDTQ) gradient [6].

4. Application

To illustrate the applicability and usefulness of our program for the evaluation of analytical QCISD(T) energy gradients we have calculated the equilibrium geometry of carbonyl oxide, CH_2OO, employing the 6-31G(d, p) basis set [12]. CH_2OO is a 1,3-dipolar species that is formed as an important intermediate during the oxidation of unsaturated hydrocarbons by ozone [13,14]. Its electronic properties are best described by the resonance structures 1–6 shown in scheme 1 [15]. Resonance structure 1 corresponds to a 1,3 π,π-biradical while resonance structures 2 and 3 describe a 1,3 zwitterion. Structures 4, 5 and 6 are probably of less importance for the wavefunction of CH_2OO [15].

Restricted HF calculations exaggerate the zwitterionic character of CH_2OO as is clearly revealed by the HF/6-31G(d, p) geometry shown in table 1. The CO bond length is rather short comparable to that found for formaldehyde, CH_2O, while the OO bond length is close to that found for OO bonds in peroxides [13,14]. Hence, the HF geometry of CH_2OO is best described by resonance structure 2.

Inclusion of correlation effects leads to a lengthening of the CO bond and a shortening of the OO bond. The resulting geometry is typical of 1,3-dipolar species with significant biradical character, i.e. correlation increases the importance of resonance structure 1. Table 1 lists geometries and energies of CH_2OO computed with analytical gradients at four different levels of theory, namely MP2 [10], MP4(SDQ) [16], MP4(SDTQ) [6], and QCISD(T). The calculated geometries differ considerably from the HF geometry. Furthermore, they reveal that the heavy atom bond lengths are very sensitive to the method used. Therefore, the predictions of the
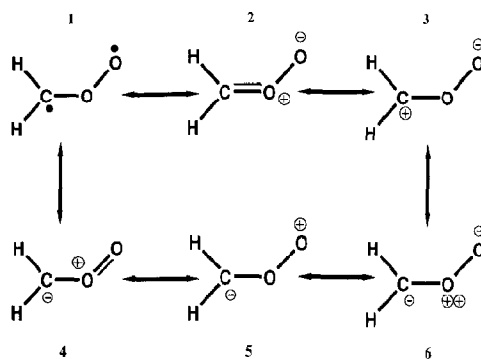
Scheme 1.

Table 1

Geometries and energies of CH_2OO calculated with the 6-31G(d, p) basis at various levels of theory [a]

Parameter	HF	MP2	MP4(SDQ)	MP4(SDTQ)	QCISD(T)
$R(CO)$	1.201	1.297	1.275	1,314	1.287
$R(OO)$	1.481	1.294	1.329	1.306	1.356
$R(CH_c)$	1.079	1.078	1.078 [b]	1.081	1.080
$R(CH_t)$	1.080	1.074	1.074 [b]	1.077	1.078
$\alpha(COO)$	114.5	120.4	119.2	119.8	119.1
$\alpha(H_cCO)$	119.7	118.2	118.6	118.3	118.8
$\alpha(H_tCO)$	118.6	114.1	115.3	114.3	115.3
E	−188.56252	−189.06865	−189.08662	−189.10975	−189.11139
$E(corr)$ [c]		−0.52467	−0.53546	−0.56846	−0.56151

[a] Bond lengths R in Å, bond angles α in deg, energies in hartree.   [b] Assumed values.

[c] $E(corr)$ denotes the calculated correlation energy.

various methods with regard to the electronic structure of CH_2OO are best discussed on the basis of the calculated heavy-atom bond lengths.

At MP2, the CO and OO bond lengths are almost identical, suggesting that biradical character (resonance structure 1) dominates the electronic structure of the molecule. This is not unexpected since MP2 is known to overestimate the biradical character of 1,3-dipolar species [14,17]. At MP4(SDQ), the CO bond is calculated to be 0.02 Å shorter and the OO bond length 0.03 Å longer than the corresponding MP2 values, reflecting the increased zwitterionic character and a stronger contribution of resonance structure 2 to the wavefunction at this level of theory.

When triple excitations are included at the MP4 level, the geometry of CH_2OO changes in an unexpected way. The alternation in the heavy-atom bond lengths is again reduced due to a lengthening of the CO bond by 0.04 Å and a shortening of the OO bond by 0.02 Å relative to the MP4(SDQ) values. In this way, the CO bond becomes slightly longer than the OO bond, indicative of an admixture of resonance structure 4 to resonance structure 1. This result contradicts the known properties of carbonyl oxides, which suggest an electronic structure of CH_2OO close to either 2 or 3.

An answer to the question as to whether the MP4(SDTQ) results are chemically relevant is given by the QCISD(T) calculations. The QCISD(T)/6-31G(d, p) energy of CH_2OO is 1.64 mhartree below that obtained at the MP4(SDTQ)/6-31G(d, p) level of theory (table 1). The QCISD(T) correlation energy is −0.56151 hartree, which has to be compared with a MP4(SDTQ) correlation energy of −0.56846 hartree. At the QCISD(T) level, the CO bond length decreases to 1.287 Å while the OO bond length increases to 1.356 Å

(table 1). Hence, the ratio of the heavy-atom bond lengths clearly predicts the importance of resonance structures **2** and **3** for the electronic structure of CH_2OO in line with the experimental observations. We conclude that the QCISD(T) description of CH_2OO is more reliable than the MP4(SDTQ) description.

Acknowledgement

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