ANALYTICAL EVALUATION OF ENERGY GRADIENTS IN QUADRATIC CONFIGURATION INTERACTION THEORY

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Analytical formulae for the energy gradient within the quadratic configuration interaction singles and doubles (QCISD) method are derived and their implementation is discussed. The method is applied to 6-31G(d) computations on H_2O and H_2O_2.

1. Introduction

Analytical methods for the evaluation of energy gradients have proven to be a powerful tool in state-of-the-art ab initio calculations. They are widely used for the characterization of potential energy surfaces [1], and in particular to locate energy minima, transition states, and reaction paths [2]. In addition the use of analytically evaluated energy derivatives facilitates the computation of vibrational spectra [3].

Analytical gradients are now routinely available for Hartree–Fock (HF) [4], MC SCF [5], and CI [6] wavefunctions. Additionally, energy gradients have been successfully implemented within second- (MP2) [7], third- (MP3) [8,9], and fourth-order singles, doubles and quadruples Møller–Plesset (MP4(SDQ)) perturbation theory [9] as well as within the coupled-cluster singles and doubles (CCSD) approach [10]. Since the potential energy surfaces and molecular properties derived from them are strongly affected by the inclusion of electron correlation, gradients for correlation corrected methods [5–10] have received particular attention.

Recently, Pople et al. [11] have introduced as a new technique for calculating correlation energies the single and double excitation quadratic CI (QCISD) approach. This method is obtained by correcting the CI equations in a simple manner to restore size consistency sacrificing the variational character of the energy. This is achieved by the inclusion of additional terms, which are quadratic in the configuration coefficients. Test calculations [11] demonstrate that the QCISD method is superior to the CI approach as well as to fourth-order MP perturbation theory. On the other hand, QCISD energies are quite close to those of the CCSD method. This is not surprising since QCISD is derived by neglecting higher-order terms in the CCSD method thus simplifying it significantly [11]. QCID is identical with CCD.

For a quantum-chemical method to be competitive, it should provide analytical techniques for the economic evaluation of energy gradients. We present in this paper the theory of analytical first QCISD energy derivatives. The implementation of the resulting final expression is discussed and the applicability of the developed programs is demonstrated by test calculations.

2. Theory

Let Ψ_0 be the HF determinantal wavefunction with n occupied spin orbitals Φ_1, ..., Φ_n, which are eigenfunctions of the Fock operator. The corresponding eigenvalues are the orbital energies ϵ_1, ..., ϵ_n. For a finite atomic orbital basis with dimension N there are in addition $N-n$ unoccupied (virtual) spin orbitals Φ_{n+1}, ...,

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Φ_N. We shall use the labels $i, j, k, \ldots$ for occupied spin orbitals, labels $a, b, c, d, \ldots$ for virtual, and labels $p, q, r, s, \ldots$ for general spin orbitals.

In QCISD theory [11] single and double excitations with respect to a given HF reference wavefunction are considered in order to account for electron correlation. The amplitudes a_i^a and a_{ij}^{ab} of these two types of excitations are determined by the QCISD equations [11]

$$(\epsilon_a-\epsilon_i)a_i^a+w(i,a)+v(i,a)=0 \tag{1a}$$

and

$$(\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j)a_{ij}^{ab}+\langle ab\|ij\rangle+w(ij,ab)+v(ij,ab)=0\,, \tag{1b}$$

where $\langle ab\|ij\rangle$ are antisymmetrized two-electron integrals

$$\langle pq\|rs\rangle=\int\int \Phi_p^*(1)\,\Phi_q^*(2)\,|r_1-r_2|^{-1}[\Phi_r(1)\Phi_s(2)-\Phi_s(1)\Phi_r(2)]\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\,. \tag{2}$$

$w(i, a)$ and $w(ij, ab)$ denote terms which are linear in the configuration coefficients a_i^a and a_{ij}^{ab}

$$w(i,a)=-\sum_j\sum_b\langle ja\|ib\rangle a_j^b-\tfrac{1}{2}\sum_j\sum_{b,c}\langle ja\|bc\rangle a_{ij}^{bc}-\tfrac{1}{2}\sum_{j,k}\sum_b\langle jk\|ib\rangle a_{jk}^{ab}\,, \tag{3a}$$

$$w(ij,ab)=\sum_c(\langle ab\|cj\rangle a_i^c-\langle ab\|ci\rangle a_j^c)+\sum_k(-\langle kb\|ij\rangle a_k^a+\langle ka\|ij\rangle a_k^b)+\tfrac{1}{2}\sum_{c,d}\langle ab\|cd\rangle a_{ij}^{cd}$$
$$+\tfrac{1}{2}\sum_{k,l}\langle kl\|ij\rangle a_{kl}^{ab}-\sum_k\sum_c(\langle kb\|jc\rangle a_{ik}^{ac}+\langle ka\|jc\rangle a_{ik}^{cb}+\langle kb\|ic\rangle a_{kj}^{ac}+\langle ka\|ic\rangle a_{kj}^{cb})\,, \tag{3b}$$

while $v(i, a)$ and $v(ij, ab)$ are quadratic arrays,

$$v(i,a)=\tfrac{1}{2}\sum_{j,k}\sum_{b,c}\langle jk\|bc\rangle(a_i^b a_{jk}^{ca}+a_j^a a_{ik}^{cb}+2a_j^b a_{ik}^{ac})\,, \tag{4a}$$

$$v(ij,ab)=\tfrac{1}{4}\sum_{k,l}\sum_{c,d}\langle kl\|cd\rangle[a_{ij}^{cd}a_{kl}^{ab}-2(a_{ij}^{ac}a_{kl}^{bd}+a_{ij}^{bd}a_{kl}^{ac})-2(a_{ik}^{ab}a_{jl}^{cd}+a_{ik}^{cd}a_{jl}^{ab})+4(a_{ik}^{ac}a_{jl}^{bd}+a_{ik}^{bd}a_{jl}^{ac})]\,. \tag{4b}$$

The QCISD equations are solved iteratively using methods from coupled-cluster theory [12,13]. The correlation energy in the QCISD approach is given by [11]

$$E(\mathrm{QCISD})=\tfrac{1}{4}\sum_{i,j}\sum_{a,b}\langle ab\|ij\rangle a_{ij}^{ab} \tag{5}$$

and involves only the coefficients a_{ij}^{ab} of the double excitations.

Differentiation of the QCISD energy expression (eq. (5)) with respect to an external perturbation parameter λ, e.g. the displacement of a nuclear coordinate or a static electric field, yields

$$\frac{\mathrm{d}E(\mathrm{QCISD})}{\mathrm{d}\lambda}=\tfrac{1}{4}\sum_{i,j}\sum_{a,b}\langle ab\|ij\rangle^{\lambda}a_{ij}^{ab}+\tfrac{1}{4}\sum_{i,j}\sum_{a,b}\langle ab\|ij\rangle\frac{\mathrm{d}a_{ij}^{ab}}{\mathrm{d}\lambda}\,, \tag{6}$$

where $\langle ij\|ab\rangle^{\lambda}$ denotes the total derivative of the two-electron integral $\langle ij\|ab\rangle$ with respect to λ. Since the QCISD energy does not obey the variation principle, the derivative amplitudes $\mathrm{d}a_{ij}^{ab}/\mathrm{d}\lambda$ have to be determined by solving the coupled-perturbed QCISD (CPQCISD) equations which are obtained by differentiating the QCISD equations (eqs. (1)) with respect to λ and which can be written in the following form (see appendix for the definitions of the B and C terms)

$$B_i^{a(\lambda)}=\sum_j\sum_b C_{i,j}^{a,b}\frac{\mathrm{d}a_j^b}{\mathrm{d}\lambda}+\sum_{j<k}\sum_{b<c}C_{i,jk}^{a,bc}\frac{\mathrm{d}a_{jk}^{bc}}{\mathrm{d}\lambda}\,, \tag{7a}$$

$$B_{ij}^{ab(\lambda)}=\sum_k\sum_c C_{ij,k}^{ab,c}\frac{\mathrm{d}a_k^c}{\mathrm{d}\lambda}+\sum_{k<l}\sum_{c<d}C_{ij,kl}^{ab,cd}\frac{\mathrm{d}a_{kl}^{cd}}{\mathrm{d}\lambda}\,. \tag{7b}$$

Explicit solution of the CPQCISD equations is very costly, because it requires for each perturbation parameter λ approximately the same time as the foregoing QCISD calculation.

Utilizing the Z-vector method of Handy and Schaefer [14] direct determination of the derivative amplitudes $\mathrm{d}a_i^a/\mathrm{d}\lambda$ and $\mathrm{d}a_{ij}^{ab}/\mathrm{d}\lambda$ can be avoided. By defining the z-amplitudes z_i^a and z_{ij}^{ab} for the QCISD approach by

$$\sum_j \sum_b z_j^b C_{j,i}^{b,a} + \sum_{j<k} \sum_{b<c} z_{jk}^{bc} C_{jk,i}^{bc,a} = 0 , \tag{8a}$$

$$\sum_k \sum_c z_k^c C_{k,ij}^{c,ab} + \sum_{k<l} \sum_{c<d} z_{kl}^{cd} C_{kl,ij}^{cd,ab} = \langle ab \| ij \rangle , \tag{8b}$$

the term in eq. (6) which depends on $\mathrm{d}a_{ij}^{ab}/\mathrm{d}\lambda$ is replaced by

$$\tfrac{1}{4} \sum_{i,j} \sum_{a,b} \langle ab \| ij \rangle \frac{\mathrm{d}a_{ij}^{ab}}{\mathrm{d}\lambda} = \sum_i \sum_a B_i^{a(\lambda)} z_i^a + \tfrac{1}{4} \sum_{i,j} \sum_{a,b} B_{ij}^{ab(\lambda)} z_{ij}^{ab} . \tag{9}$$

The advantage of the Z-vector method is that only one coupled system of linear equations has to be solved in order to determine z_i^a and z_{ij}^{ab}. The cost is similar to that for the solution of the QCISD equations.

The final expression for the QCISD energy gradient is then given by

$$\begin{aligned}
\frac{\mathrm{d}E(\mathrm{QCISD})}{\mathrm{d}\lambda} &= \tfrac{1}{4} \sum_{i,j} \sum_{a,b} \langle ij \| ab \rangle^{\lambda} a_{ij}^{ab} + \sum_i \sum_a B_i^{a(\lambda)} z_i^a + \tfrac{1}{4} \sum_{i,j} \sum_{a,b} B_{ij}^{ab(\lambda)} z_{ij}^{ab} \\
&= \tfrac{1}{4} \sum_{i,j} \sum_{a,b} \langle ij \| ab \rangle^{\lambda} (a_{ij}^{ab} - z_{ij}^{ab} - x_{ij}^{ab}) \\
&\quad - \tfrac{1}{8} \sum_{i,j} \sum_{a,b} z_{ij}^{ab} \Bigg(\sum_{c,d} \langle ab \| cd \rangle^{\lambda} a_{ij}^{cd} + \sum_{k,l} \langle kl \| ij \rangle^{\lambda} a_{kl}^{ab} \\
&\quad - \sum_k \sum_c 2 (\langle kb \| jc \rangle^{\lambda} a_{ik}^{ac} + \langle ka \| jc \rangle^{\lambda} a_{ik}^{cb} + \langle kb \| ic \rangle^{\lambda} a_{kj}^{ac} + \langle ka \| ic \rangle^{\lambda} a_{kj}^{cb}) \Bigg) \\
&\quad + \sum_{i,j} \sum_{a,b} \langle ja \| ib \rangle^{\lambda} z_i^a a_j^b + \tfrac{1}{2} \sum_{i,j} \sum_{a,b,c} \langle ja \| bc \rangle^{\lambda} (a_{ij}^{bc} z_i^a + z_{ij}^{bc} a_i^a) \\
&\quad + \tfrac{1}{2} \sum_{i,j,k} \sum_{a,b} \langle jk \| ib \rangle^{\lambda} (a_{jk}^{ab} z_i^a + z_{jk}^{ab} a_i^a) - \sum_{a,c} \frac{\partial \epsilon_{ac}}{\partial \lambda} \Bigg(\sum_i a_i^c z_i^a + \tfrac{1}{2} \sum_{i,j} \sum_b a_{ij}^{cb} z_{ij}^{ab} \Bigg) \\
&\quad + \sum_{i,k} \frac{\partial \epsilon_{ik}}{\partial \lambda} \Bigg(\sum_a a_k^a z_i^a + \tfrac{1}{2} \sum_j \sum_{a,b} a_{kj}^{ab} z_{ij}^{ab} \Bigg) ,
\end{aligned} \tag{10}$$

where x_{ij}^{ab} is defined as

$$\begin{aligned}
x_{ij}^{ab} &= \sum_k \sum_c z_k^c (a_{ij}^{ca} a_k^b - a_{ij}^{cb} a_k^a + a_{jk}^{ab} a_i^c - a_{ik}^{ab} a_j^c + a_{jk}^{bc} a_i^a - a_{jk}^{ac} a_i^b - a_{ik}^{bc} a_j^a + a_{ik}^{ac} a_j^b) \\
&\quad + \tfrac{1}{4} \sum_{k,l} \sum_{c,d} z_{kl}^{cd} [a_{ij}^{cd} a_{kl}^{ab} - 2 (a_{ij}^{ac} a_{kl}^{bd} + a_{ij}^{bd} a_{kl}^{ac}) - 2 (a_{ik}^{ab} a_{jl}^{cd} + a_{ik}^{cd} a_{jl}^{ab}) + 4 (a_{ik}^{ac} a_{jl}^{bd} + a_{ik}^{bd} a_{jl}^{ac})] .
\end{aligned} \tag{11}$$

Since QCISD can be derived by neglecting several higher-order terms in the CCSD approach, an expression for the QCISD energy gradient can be obtained alternatively by neglecting the corresponding terms in the CCSD energy gradient expression [10,15].

The total derivatives $\langle pq \| rs \rangle^{\lambda}$ of the MO two-electron integrals are given within standard coupled-perturbed HF (CPHF) theory [16] as

$$\langle pq\|rs\rangle^{\lambda} = \sum_{\mu,\nu,\sigma,\rho} c_{\mu p} c_{\nu q} c_{\sigma r} c_{\rho s} \langle \mu\nu\|\sigma\rho\rangle^{\lambda}$$

$$+ \sum_{t} \left(U^{\lambda}_{tp} \langle tq\|rs\rangle + U^{\lambda}_{tq} \langle pt\|rs\rangle + U^{\lambda}_{tr} \langle pq\|ts\rangle + U^{\lambda}_{ts} \langle pq\|rt\rangle \right), \tag{12}$$

where $\langle \mu\nu\|\sigma\rho\rangle^{\lambda}$ denotes the derivatives of the AO two-electron integrals with respect to λ and where U^{λ}_{pq} are the first-order changes in the MO coefficients $c_{\mu q}$. These coefficients are obtained by solving the CPHF equations [16]. Eq. (10) for the QCISD energy gradient can be rearranged into the following form:

$$\frac{dE(\mathrm{QCISD})}{d\lambda} = \sum_{\mu,\nu,\sigma,\rho} T_{\mu\nu\sigma\rho} \langle \mu\nu\|\sigma\rho\rangle^{\lambda} + \sum_{i} \sum_{a} \left(U^{\lambda}_{ai} L'_{ia} + U^{\lambda}_{ia} L''_{ai} \right)$$

$$+ \sum_{i,j} \left(-\tfrac{1}{2} S^{\lambda}_{ij} L'_{ij} + \frac{\partial \epsilon_{ij}}{\partial \lambda} K'_{ij} \right) + \sum_{a,b} \left(-\tfrac{1}{2} S^{\lambda}_{ab} L''_{ab} + \frac{\partial \epsilon_{ab}}{\partial \lambda} K''_{ab} \right), \tag{13}$$

where S^{λ}_{pq} denotes the AO overlap integral derivatives rotated into the MO basis. The factors $T_{\mu\nu\sigma\rho}$, L'_{pi}, L''_{pa}, K'_{ij}, and K''_{ab} in eq. (13) are independent of the perturbation parameter λ and are easily obtained by substituting eq. (12) into eq. (10). We note further that solution of the CPHF equations can be avoided by using the Z-vector method of Handy and Schaefer [14]. A full account of the elimination of the coefficients U^{λ}_{ai} from the gradient expressions for correlated wavefunctions is given in refs. [9,17].

3. Implementation

Computer programs for the analytical evaluation of QCISD energy gradients based on eqs. (10) and (13) have been written for the program system COLOGNE [18] [#1]. The steps required for a gradient calculation as currently implemented are as follows:

(1) The one- and two-electron integrals are evaluated in the atomic orbital basis.

(2) The SCF procedure is carried out to obtain the HF reference wavefunction.

(3) The two-electron integrals are transformed into the MO basis.

(4) The amplitudes a^{a}_{i} and a^{ab}_{ij} are determined by iteratively solving the QCISD equations. Convergence is accelerated using a DIIS procedure [13].

(5) The Z-vector equation of the CPQCISD theory is iteratively solved in order to evaluate z^{a}_{i} and z^{ab}_{ij}.

(6) The derivatives of the one-electron integrals are computed and stored.

(7) The prefactors $T_{\mu\nu\sigma\rho}$ of the AO two-electron integral derivatives are calculated in the MO basis, transformed into the AO basis, and sorted according to the different shell combinations [9].

(8) The two-electron integral derivatives $\langle \mu\nu\|\sigma\rho\rangle^{\lambda}$ are formed and immediately contracted with the appropriate prefactor $T_{\mu\nu\sigma\rho}$.

(9) The factors L'_{pi}, L''_{pa}, K'_{ij}, and K''_{ab} are computed and stored.

(10) The CPHF equations are solved for U^{λ}_{ai} and all contributions to the QCISD energy gradient are summed up.

The solution of the QCISD as well as the Z-vector equations requires $O(n^2(N-n)^4)$ multiplication per iteration. In the subsequent gradient evaluation, transformation of the elements $T_{\mu\nu\sigma\rho}$ from the MO into the AO basis involves $O(N^5)$ operations in the most expensive step. Depending on the ratio n/N, timings for the QCISD gradient calculation are similar to those of the preceding energy calculation.

Coupled-cluster doubles (CCD) gradients [20] can be evaluated within the same program by omitting all contributions due to single excitations.

To illustrate the applicability of the implemented computer programs, we have calculated the equilibrium geometry for H_2O at the QCISD level using analytically evaluated gradients using the 6-31G(d) [21] and a

[#1] COLOGNE is a program system developed for a CDC Cyber 176 computer and contains parts of GAUSSIAN 82 [19].

Table 1
Theoretical geometries, energies, dipole moments, harmonic vibrational frequencies, and infrared intensities of H_2O using analytical gradients [a]

	HF		CCD		QCISD		Experimental [b]
	6-31G(d)	TZ+2P	6-31G(d)	TZ+2P	6-31G(d)	TZ+2P	
r_{OH}	0.947	0.941	0.968	0.956	0.969	0.957	0.958
α_{HOH}	105.5	106.1	104.2	104.5	104.2	104.5	104.5
E	−76.01075	−76.05251	−76.20740	−76.31120	−76.20821	−76.31276	-
μ	2.199	-	2.183	-	2.178	-	1.85
ν_1	4189	-	3901	-	3879	-	3756 (3942)
ν_2	4071	-	3776	-	3753	-	3657 (3832)
ν_3	1827	-	1746	-	1744	-	1595 (1648)
I_1	58.1	-	27.4	-	24.7	-	44.6
I_2	18.2	-	3.7	-	2.8	-	2.2
I_3	107.3	-	87.7	-	85.6	-	53.6

[a] Energies in hartree, distances in Å, angles in deg, dipole moment μ in D, vibrational frequencies ν in cm^{-1}, and intensities I in km/mol.

[b] 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_2O_2 [a]

	HF/6-31G(d) [b]	MP4(SDQ)/6-31G(d) [c]	QCISD/6-31G(d)
r_{OO}	1.397	1.464	1.464
r_{OH}	0.949	0.974	0.975
α_{OOH}	102.1	99.3	99.4
τ_{HOOH}	116.0	120.9	120.8
E	−150.76479	−1.51.14689	−151.14775

[a] Energies in hartree, distances in Å, and angles in deg. [b] Ref. [28]. [c] Ref. [9].

[5s3p2d/3s2p] Dunning–Huzinaga basis set (TZ+2P) [22] [#2] (see table 1). In addition, QCISD/6-31G(d) gradients have been used to obtain harmonic frequencies and infrared intensities, which are also shown in table 1. These data indicate that molecular properties with spectroscopic accuracy can be obtained at the QCISD level provided a sufficiently large basis set is used. In another application the equilibrium geometry of H_2O_2 has been calculated at the QCISD/6-31G(d) level (see table 2). Using the MP4(SDQ)/6-31G(d) geometry for H_2O_2 [9] as an initial guess the optimization converged in two cycles, indicating that both levels of theory lead to similar improvements compared to the HF geometry [28].

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[#2] The exponents of the polarization functions in the TZ+2P basis were $\alpha_{d1}(O)=1.5$, $\alpha_{d2}(O)=0.5$, $\alpha_{p1}(H)=1.5$, and $\alpha_{p2}(H)=0.5$.

Appendix

The various terms in the CPQCISD equations (eqs. (7)) are given by

$$B_i^{a(\lambda)} = -\sum_b \frac{\partial \epsilon_{ab}}{\partial \lambda} a_i^b + \sum_j \frac{\partial \epsilon_{ij}}{\partial \lambda} a_j^a + \sum_j \sum_b \langle ja \| ib \rangle^\lambda a_j^b + \tfrac{1}{2} \sum_j \sum_{b,c} \langle ja \| bc \rangle^\lambda a_{ij}^{bc}$$
$$+ \tfrac{1}{2} \sum_{j,k} \sum_b \langle jk \| ib \rangle^\lambda a_{jk}^{ab} - \tfrac{1}{2} \sum_{j,k} \sum_{b,c} \langle jk \| ib \rangle^\lambda (a_i^b a_{jk}^{ca} + a_j^a a_{ik}^{cb} + 2 a_j^b a_{ik}^{ac}) , \tag{A.1}$$

$$B_{ij}^{ab(\lambda)} = -\langle ab \| ij \rangle^\lambda - \sum_c \left(\frac{\partial \epsilon_{ac}}{\partial \lambda} a_{ij}^{cb} + \frac{\partial \epsilon_{bc}}{\partial \lambda} a_{ij}^{ac} \right) + \sum_k \left(\frac{\partial \epsilon_{ik}}{\partial \lambda} a_{kj}^{ab} + \frac{\partial \epsilon_{jk}}{\partial \lambda} a_{ik}^{ab} \right)$$
$$- \tfrac{1}{2} \sum_{c,d} \langle ab \| cd \rangle^\lambda a_{ij}^{cd} - \tfrac{1}{2} \sum_{k,l} \langle kl \| ij \rangle^\lambda a_{kl}^{ab}$$
$$+ \sum_k \sum_c (\langle kb \| jc \rangle^\lambda a_{ik}^{ac} + \langle ka \| jc \rangle^\lambda a_{ik}^{cb} + \langle kb \| ic \rangle^\lambda a_{kj}^{ac} + \langle ka \| ic \rangle^\lambda a_{kj}^{cb})$$
$$- \tfrac{1}{4} \sum_{k,l} \sum_{c,d} \langle kl \| cd \rangle^\lambda [a_{ij}^{cd} a_{kl}^{ab} - 2(a_{ij}^{ac} a_{kl}^{bd} + a_{ij}^{bd} a_{kl}^{ac})$$
$$- 2(a_{ik}^{ab} a_{jl}^{cd} + a_{ik}^{cd} a_{jl}^{ab}) + 4(a_{ik}^{ac} a_{jl}^{bd} + a_{ik}^{bd} a_{jl}^{ac})]$$
$$- \sum_c (\langle ab \| cj \rangle^\lambda a_i^c - \langle ab \| ci \rangle^\lambda a_j^c) - \sum_k (-\langle kb \| ij \rangle^\lambda a_k^a + \langle ka \| ij \rangle^\lambda a_k^b) , \tag{A.2}$$

$$\sum_j \sum_b C_{i,j}^{a,b} \frac{\mathrm{d}a_j^b}{\mathrm{d}\lambda} = (\epsilon_a - \epsilon_i) \frac{\mathrm{d}a_i^a}{\mathrm{d}\lambda} - \sum_j \sum_b \langle ja \| ib \rangle \frac{\mathrm{d}a_j^b}{\mathrm{d}\lambda}$$
$$+ \tfrac{1}{2} \sum_{j,k} \sum_{b,c} \langle jk \| bc \rangle \left(a_{jk}^{ca} \frac{\mathrm{d}a_i^b}{\mathrm{d}\lambda} + a_{ik}^{cb} \frac{\mathrm{d}a_j^a}{\mathrm{d}\lambda} + 2 a_{ik}^{ac} \frac{\mathrm{d}a_j^b}{\mathrm{d}\lambda} \right) , \tag{A.3}$$

$$\sum_{j<k} \sum_{b<c} C_{i,jk}^{a,bc} \frac{\mathrm{d}a_{jk}^{bc}}{\mathrm{d}\lambda} = -\tfrac{1}{2} \sum_j \sum_{b,c} \langle ja \| bc \rangle \frac{\mathrm{d}a_{ij}^{bc}}{\mathrm{d}\lambda} - \tfrac{1}{2} \sum_{j,k} \sum_b \langle jk \| ib \rangle \frac{\mathrm{d}a_{jk}^{ab}}{\mathrm{d}\lambda}$$
$$+ \tfrac{1}{2} \sum_{j,k} \sum_{b,c} \langle jk \| bc \rangle \left(\frac{\mathrm{d}a_{jk}^{ca}}{\mathrm{d}\lambda} a_i^b + \frac{\mathrm{d}a_{ik}^{cb}}{\mathrm{d}\lambda} a_j^a + 2 \frac{\mathrm{d}a_{ik}^{ac}}{\mathrm{d}\lambda} a_j^b \right) , \tag{A.4}$$

$$\sum_k \sum_c C_{ij,k}^{ab,c} \frac{\mathrm{d}a_k^c}{\mathrm{d}\lambda} = \sum_c \left(\langle ab \| cj \rangle \frac{\mathrm{d}a_i^c}{\mathrm{d}\lambda} - \langle ab \| ci \rangle \frac{\mathrm{d}a_j^c}{\mathrm{d}\lambda} \right) + \sum_k \left(-\langle kb \| ij \rangle \frac{\mathrm{d}a_k^a}{\mathrm{d}\lambda} + \langle ka \| ij \rangle \frac{\mathrm{d}a_k^b}{\mathrm{d}\lambda} \right) , \tag{A.5}$$

$$\sum_{k<l} \sum_{c<d} C_{ij,kl}^{ab,cd} \frac{\mathrm{d}a_{kl}^{cd}}{\mathrm{d}\lambda} = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) \frac{\mathrm{d}a_{ij}^{ab}}{\mathrm{d}\lambda} + \tfrac{1}{2} \sum_{c,d} \langle ab \| cd \rangle \frac{\mathrm{d}a_{ij}^{cd}}{\mathrm{d}\lambda} + \tfrac{1}{2} \sum_{k,l} \langle kl \| ij \rangle \frac{\mathrm{d}a_{kl}^{ab}}{\mathrm{d}\lambda}$$
$$- \sum_k \sum_c \left(\langle kb \| jc \rangle \frac{\mathrm{d}a_{ik}^{ac}}{\mathrm{d}\lambda} + \langle ka \| jc \rangle \frac{\mathrm{d}a_{ik}^{cb}}{\mathrm{d}\lambda} + \langle kb \| ic \rangle \frac{\mathrm{d}a_{kj}^{ac}}{\mathrm{d}\lambda} + \langle ka \| ic \rangle \frac{\mathrm{d}a_{kj}^{cb}}{\mathrm{d}\lambda} \right)$$
$$+ \tfrac{1}{4} \sum_{k,l} \sum_{c,d} \langle kl \| cd \rangle \left[\frac{\mathrm{d}a_{ij}^{cd}}{\mathrm{d}\lambda} a_{kl}^{ab} + a_{ij}^{cd} \frac{\mathrm{d}a_{kl}^{ab}}{\mathrm{d}\lambda} - 2 \left(a_{ij}^{ac} \frac{\mathrm{d}a_{kl}^{bd}}{\mathrm{d}\lambda} + a_{ij}^{bd} \frac{\mathrm{d}a_{kl}^{ac}}{\mathrm{d}\lambda} + \frac{\mathrm{d}a_{ij}^{ac}}{\mathrm{d}\lambda} a_{kl}^{bd} + \frac{\mathrm{d}a_{ij}^{bd}}{\mathrm{d}\lambda} a_{kl}^{ac} \right) \right.$$
$$- 2 \left(a_{ik}^{ab} \frac{\mathrm{d}a_{jl}^{cd}}{\mathrm{d}\lambda} + a_{ik}^{cd} \frac{\mathrm{d}a_{jl}^{ab}}{\mathrm{d}\lambda} + \frac{\mathrm{d}a_{ik}^{ab}}{\mathrm{d}\lambda} a_{jl}^{cd} + \frac{\mathrm{d}a_{ik}^{cd}}{\mathrm{d}\lambda} a_{jl}^{ab} \right)$$
$$\left. + 4 \left(a_{ik}^{ac} \frac{\mathrm{d}a_{jl}^{bd}}{\mathrm{d}\lambda} + a_{ik}^{bd} \frac{\mathrm{d}a_{jl}^{ac}}{\mathrm{d}\lambda} + \frac{\mathrm{d}a_{ik}^{ac}}{\mathrm{d}\lambda} a_{jl}^{bd} + \frac{\mathrm{d}a_{ik}^{bd}}{\mathrm{d}\lambda} a_{jl}^{ac} \right) \right] . \tag{A.6}$$

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