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Citation: *The Journal of Chemical Physics* **139**, 154106 (2013); doi: 10.1063/1.4824715

View online: <http://dx.doi.org/10.1063/1.4824715>

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Analytic evaluation of the dipole Hessian matrix in coupled-cluster theory

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(Received 9 August 2013; accepted 26 September 2013; published online 17 October 2013)

The general theory required for the calculation of analytic third energy derivatives at the coupled-cluster level of theory is presented and connected to preceding special formulations for hyperpolarizabilities and polarizability gradients. Based on our theory, we have implemented a scheme for calculating the dipole Hessian matrix in a fully analytical manner within the coupled-cluster singles and doubles approximation. The dipole Hessian matrix is the second geometrical derivative of the dipole moment and thus a third derivative of the energy. It plays a crucial role in IR spectroscopy when taking into account anharmonic effects and is also essential for computing vibrational corrections to dipole moments. The superior accuracy of the analytic evaluation of third energy derivatives as compared to numerical differentiation schemes is demonstrated in some pilot calculations.

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I. INTRODUCTION

An important area of research in quantum chemistry is the development of schemes for the determination of molecular properties as they provide the link to a variety of experimental data.^{1,2} While molecular equilibrium structures and a range of first-order properties can be determined by means of energy gradients, second derivatives of the energy provide access to vibrational frequencies and infrared intensities³ within the harmonic approximation as well as other second-order properties. Third- and higher-order energy derivatives are of importance, for example, when studying nonlinear optical properties⁴ or vibrational spectra beyond the harmonic approximation.^{5,6}

The simplest approach to calculate molecular properties is through numerical differentiation of the energy, but analytic derivatives are superior for a number of reasons:

- The accuracy of analytic derivatives is, in principle, equal to that of the undifferentiated parent quantity, whereas numerical derivatives suffer from a discretization error resulting from approximating derivatives by finite differences as well as a rounding error due to all quantities being determined and processed with limited precision. Choosing the right step size for the numerical differentiation is crucial in order to minimize the overall error, but this is not always easy and in some cases, no step size leads to results of acceptable accuracy.⁷ This problem becomes evident especially when seeking higher than first derivatives.
- As a consequence of the $2n + 1$ and $2n + 2$ rules of derivative theory,^{8–10} analytic derivatives are superior in terms of computational cost. As a general rule, the purely numerical calculation of the n -th deriva-

tive scales as N_{pert}^n with N_{pert} as the number of perturbations, while the analytical evaluation scales as $N_{\text{pert}}^{(n-1)/2}$ and $N_{\text{pert}}^{n/2}$ for odd and even derivatives, respectively. Mixed numerical-analytical differentiation schemes entail intermediate cost, but are not superior to the fully analytical evaluation.

- Analytic derivatives can be evaluated more easily in a black-box manner as compared to approaches involving numerical differentiation steps, where one might face difficulties in describing the desired states with sufficient accuracy.
- Analytic-derivative theory can be extended to time-dependent and magnetic perturbations.^{1,11} In contrast, the calculation of frequency-dependent properties is not straightforward when using numerical differentiation and the calculation of magnetic properties via numerical schemes is also rather involved as it requires complex algebra.¹²

Molecular properties have been determined using a variety of quantum-chemical methods, among which coupled-cluster (CC) theory^{13,14} (for a recent overview, see Ref. 15) stands out due to its high accuracy and reliability. Analytic first^{16–18} and second^{19–22} derivatives are nowadays used in a routine manner in CC theory, but only selected third- and higher-order CC energy derivatives have yet been calculated analytically. Noteworthy achievements in this regard are implementations of first^{23–25} and second²⁶ hyperpolarizabilities, Verdet constants,^{27,28} and polarizability gradients.²⁹ We note that corresponding developments for Hartree-Fock (HF) theory^{30–36} and more recently also for density-functional theory (DFT)^{37–41} have been reported as well. Furthermore, it is worth mentioning that theoretical expressions for general third derivatives of the HF energy were presented more than 30 years ago^{8,42} and analytic cubic^{43–46} and quartic⁴⁷ force constants as well as mixed electric-geometrical derivatives up to fourth order⁴⁸ were implemented for HF wave functions

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more than 20 years ago. The corresponding achievements at the DFT level have been reported recently.⁴⁹ As regards extensions to correlated wave-function based methods, theoretical expressions for third-order energy derivatives at the second-order Møller-Plesset⁹ (MP2) and the CC¹⁹ level of theory were reported but have never been implemented. Instead, numerical differentiation of analytic first or second derivatives has commonly been used for the calculation of these quantities.^{22,50,51} Furthermore, it has been common practice to evaluate anharmonic contributions at a lower level of theory than the corresponding harmonic force field,⁵² which often leads to acceptable results, but is not entirely satisfying from a rigorous point of view.

In this article, we derive the theory for general analytic third derivatives in the CC framework. In addition, we present a first implementation for the analytic evaluation of the dipole Hessian matrix for CC theory with singles and doubles excitations (CCSD)⁵³ as well as MP2 theory.⁵⁴ The dipole Hessian matrix is obtained by differentiating the energy once with respect to an external electric field and twice with respect to displacements of the nuclei. It is of importance for the determination of infrared intensities when considering anharmonic effects as it contributes to the so-called electrical anharmonicity⁵⁵ and also delivers a contribution to the vibrationally averaged dipole moment.⁵⁶

The article is structured as follows: We begin with the derivation of a general expression for the third derivative of the CC energy in Section II. Section III deals with some details of our implementation, while Section IV features pilot applications, in which we compare numerical and analytical differentiation schemes with respect to their accuracy. Section V finally presents some concluding remarks.

II. THEORY

In CC theory,¹⁵ the wave function is parametrized in an exponential fashion as

$$|\Psi\rangle = e^{\hat{T}} |\Psi_0\rangle \quad (1)$$

with Ψ_0 as reference wave function – which is usually chosen as the HF wave function – and \hat{T} as the cluster operator. The latter is defined as

$$\begin{aligned} \hat{T} &= \hat{T}_1 + \hat{T}_2 + \dots \\ &= \sum_a \sum_i t_i^a \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4} \sum_{ab} \sum_{ij} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \dots, \quad (2) \end{aligned}$$

where \hat{a}^\dagger and \hat{a} represent the usual second-quantized creation and annihilation operators and i, j, \dots and a, b, \dots stand for occupied and virtual spin orbitals, respectively. The energy is computed from the projection of the Schrödinger equation on the reference wave function

$$E = \langle \Psi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle, \quad (3)$$

whereas the cluster amplitudes $t_{ij}^{ab\dots}$ are determined from the equations obtained via projection on the excited determinants according to

$$0 = \langle \Psi_{ij\dots}^{ab\dots} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle. \quad (4)$$

When deriving an expression for the third derivative of the CC energy, it is preferable to start from an appropriate Lagrangian^{9,10,19,57,58} in order to take advantage of the $2n + 1$ and $2n + 2$ rules of derivative theory, i.e., the fact that wave function parameters and Lagrange multipliers of order n determine the derivatives of the energy up to order $2n + 1$ and $2n + 2$, respectively. The CC Lagrangian reads

$$\mathcal{L} = \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \quad (5)$$

with the Λ operator defined as

$$\begin{aligned} \hat{\Lambda} &= \hat{\Lambda}_1 + \hat{\Lambda}_2 + \dots \\ &= \sum_a \sum_i \lambda_a^i \hat{a}_i^\dagger \hat{a}_a + \frac{1}{4} \sum_{ab} \sum_{ij} \lambda_{ab}^{ij} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \dots. \quad (6) \end{aligned}$$

The Lagrange multipliers $\lambda_{ab\dots}^{ij\dots}$ are determined from the stationarity condition

$$\frac{\partial \mathcal{L}}{\partial t_{ij\dots}^{ab\dots}} = 0. \quad (7)$$

Equation (5) takes into account the non-variational nature of CC theory, but in addition, one must deal with the dependence of the CC energy on the molecular orbitals (MOs) if the response of the reference wave function to the perturbation (known as orbital relaxation) is considered. To this end, the Brillouin condition and the orthonormality of the MOs are included as additional constraints in Eq. (5), which leads to¹⁹

$$\begin{aligned} \mathcal{L} &= \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle \\ &+ \sum_{ai} Z_{ai} f_{ai} + \sum_{pq} I_{pq} (S_{pq} - \delta_{pq}), \quad (8) \end{aligned}$$

where the additional Lagrange multipliers Z_{ai} and I_{pq} are the Z -vector⁵⁹ and the energy-weighted density matrix, respectively. p, q, \dots refer here to generic orbitals and f_{pq} and S_{pq} denote the usual Fock-matrix and overlap-matrix elements in the MO representation. In principle, Eq. (8) is a valid starting point for the formulation of analytic derivatives. However, from the point of view of implementation, it is advantageous to resort to a density-matrix-based formulation.⁶⁰ This yields for the Lagrangian in Eq. (8)

$$\begin{aligned} \mathcal{L} &= \sum_{pq} D_{pq} f_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle pq || rs \rangle \\ &+ \sum_{ai} Z_{ai} f_{ai} + \sum_{pq} I_{pq} (S_{pq} - \delta_{pq}), \quad (9) \end{aligned}$$

where the elements of the one-particle and two-particle density matrices are given as

$$D_{pq} = \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \{ \hat{a}_p^\dagger \hat{a}_q \} e^{\hat{T}} | \Psi_0 \rangle, \quad (10)$$

$$\Gamma_{pqrs} = \frac{1}{4} \langle \Psi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \{ \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \} e^{\hat{T}} | \Psi_0 \rangle \quad (11)$$

and $\langle pq || rs \rangle$ denotes the antisymmetrized two-electron integrals. We note that Eq. (9) holds for MP2 theory as well.

Differentiating the Lagrangian in Eq. (9) three times with respect to arbitrary perturbations χ_1, χ_2 , and χ_3 while bearing in mind the $2n + 1$ and $2n + 2$ rules yields for the third derivative of the CC energy

$$\begin{aligned}
\frac{d^3 E}{d\chi_1 d\chi_2 d\chi_3} &= \frac{\partial^3 \mathcal{L}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} = \sum_{pq} D_{pq} \left(\frac{\partial^3 f_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} + \sum_{pqrs} \Gamma_{pqrs} \left(\frac{\partial^3 \langle pq||rs \rangle}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} \\
&+ \sum_{pq} I_{pq} \left(\frac{\partial^3 S_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} + \sum_{ai} Z_{ai} \left(\frac{\partial^3 f_{ai}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} \\
&+ P_{123}^3 \left[\sum_{pq} \frac{\partial D_{pq}}{\partial \chi_1} \left(\frac{\partial^2 f_{pq}}{\partial \chi_2 \partial \chi_3} \right)^{(1)} + \sum_{pqrs} \frac{\partial \Gamma_{pqrs}}{\partial \chi_1} \left(\frac{\partial^2 \langle pq||rs \rangle}{\partial \chi_2 \partial \chi_3} \right)^{(1)} \right. \\
&+ \left. \sum_{pq} \frac{\partial I_{pq}}{\partial \chi_1} \left(\frac{\partial^2 S_{pq}}{\partial \chi_2 \partial \chi_3} \right)^{(1)} + \sum_{ai} \frac{\partial Z_{ai}}{\partial \chi_1} \left(\frac{\partial^2 f_{ai}}{\partial \chi_2 \partial \chi_3} \right)^{(1)} \right] \\
&+ P_{123}^3 \left[\sum_{pq} \left(\frac{\partial^2 D_{pq}}{\partial \chi_1 \partial \chi_2} \right)^{(1,1)} \frac{\partial f_{pq}}{\partial \chi_3} + \sum_{pqrs} \left(\frac{\partial^2 \Gamma_{pqrs}}{\partial \chi_1 \partial \chi_2} \right)^{(1,1)} \frac{\partial \langle pq||rs \rangle}{\partial \chi_3} \right] \\
&+ \sum_{pqrs} \left(\frac{\partial^3 \Gamma_{pqrs}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1,1)} \langle pq||rs \rangle
\end{aligned} \tag{12}$$

with P_{123}^3 invoking a cyclic permutation of the perturbations χ_1 , χ_2 , and χ_3 . In order to obtain a compact expression, we have made use of the notation introduced in Refs. 25 and 29 for the higher-order derivatives of the density matrices, Fock matrices, and two-electron integrals. The notation

$$\left(\frac{\partial^n D}{\partial \chi_1 \partial \chi_2 \dots} \right)^{(1,1)} \tag{13}$$

indicates that at most the first derivative of the cluster amplitudes $t_{ij\dots}^{ab\dots}$ and Lagrange multipliers $\lambda_{ab\dots}^{ij\dots}$ contributes to the derivative of the density matrix D , whereas the Fock-matrix derivative

$$\left(\frac{\partial^n f}{\partial \chi_1 \partial \chi_2 \dots} \right)^{(1)} \tag{14}$$

contains coupled-perturbed Hartree-Fock (CPHF) coefficients⁶¹ of at most first order. Similar definitions hold for the derivatives of the two-electron terms. Also, we note that the second and third restricted derivatives of the two-particle density matrix vanish for MP2.

The exact expressions for the derivatives of D , Γ , and I depend on the underlying wave function. However, they can be obtained in a straightforward manner from the corresponding unperturbed quantities. The second and third derivatives of the Fock matrix are conveniently split into a one-electron and a two-electron part according to

$$\left(\frac{\partial^2 f_{pq}}{\partial \chi_1 \partial \chi_2} \right)^{(1)} = \left(\frac{\partial^2 h_{pq}}{\partial \chi_1 \partial \chi_2} \right)^{(1)} + \sum_j \left(\frac{\partial^2 \langle pj||qj \rangle}{\partial \chi_1 \partial \chi_2} \right)^{(1)}, \tag{15}$$

$$\begin{aligned}
&\left(\frac{\partial^3 f_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} \\
&= \left(\frac{\partial^3 h_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} + \sum_j \left(\frac{\partial^3 \langle pj||qj \rangle}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)}.
\end{aligned} \tag{16}$$

The required derivatives of the one-electron Hamiltonian are given as

$$\begin{aligned}
&\left(\frac{\partial^2 h_{pq}}{\partial \chi_1 \partial \chi_2} \right)^{(1)} \\
&= h_{pq}^{\chi_1 \chi_2} + P_{12} \left[\sum_r (U_{rq}^{\chi_1} h_{pr}^{\chi_2} + U_{rp}^{\chi_1} h_{rq}^{\chi_2}) + \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} h_{rs} \right],
\end{aligned} \tag{17}$$

$$\begin{aligned}
&\left(\frac{\partial^3 h_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3} \right)^{(1)} = h_{pq}^{\chi_1 \chi_2 \chi_3} + P_{123}^3 \sum_r (U_{rq}^{\chi_1} h_{pr}^{\chi_2 \chi_3} + U_{rp}^{\chi_1} h_{rq}^{\chi_2 \chi_3}) \\
&+ P_{123}^6 \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} h_{rs}^{\chi_3},
\end{aligned} \tag{18}$$

where $h_{pq}^{\chi_1}$, $h_{pq}^{\chi_1 \chi_2}$, and $h_{pq}^{\chi_1 \chi_2 \chi_3}$ denote the first, second, and third derivatives of the one-electron atomic-orbital (AO) integrals rotated into the MO basis and $U_{pq}^{\chi_i}$ denotes the CPHF coefficients corresponding to perturbation χ_i . P_{123}^6 invokes the full set of permutations of χ_1 , χ_2 , and χ_3 and P_{12} the permutation of χ_1 and χ_2 . The derivatives of the two-electron integrals become

$$\begin{aligned} \left(\frac{\partial^2 \langle pq||rs \rangle}{\partial \chi_1 \partial \chi_2}\right)^{(1)} &= \langle pq||rs \rangle^{\chi_1 \chi_2} \\ &+ P_{12} \left[\sum_t (U_{tp}^{\chi_1} \langle tq||rs \rangle^{\chi_2} + U_{tq}^{\chi_1} \langle pt||rs \rangle^{\chi_2} + U_{tr}^{\chi_1} \langle pq||ts \rangle^{\chi_2} + U_{ts}^{\chi_1} \langle pq||rt \rangle^{\chi_2}) \right] \\ &+ P_{12} \left[\sum_{tu} (U_{tp}^{\chi_1} U_{uq}^{\chi_2} \langle tu||rs \rangle + U_{tp}^{\chi_1} U_{ur}^{\chi_2} \langle tq||us \rangle + U_{tp}^{\chi_1} U_{us}^{\chi_2} \langle tq||ru \rangle \right. \\ &\quad \left. + U_{tq}^{\chi_1} U_{ur}^{\chi_2} \langle pt||us \rangle + U_{tq}^{\chi_1} U_{us}^{\chi_2} \langle pt||ru \rangle + U_{tr}^{\chi_1} U_{us}^{\chi_2} \langle pq||tu \rangle) \right], \end{aligned} \quad (19)$$

$$\begin{aligned} \left(\frac{\partial^3 \langle pq||rs \rangle}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} &= \langle pq||rs \rangle^{\chi_1 \chi_2 \chi_3} \\ &+ P_{123}^3 \left[\sum_t (U_{tp}^{\chi_1} \langle tq||rs \rangle^{\chi_2 \chi_3} + U_{tq}^{\chi_1} \langle pt||rs \rangle^{\chi_2 \chi_3} \right. \\ &\quad \left. + U_{tr}^{\chi_1} \langle pq||ts \rangle^{\chi_2 \chi_3} + U_{ts}^{\chi_1} \langle pq||rt \rangle^{\chi_2 \chi_3}) \right] \\ &+ P_{123}^6 \left[\sum_{tu} (U_{tp}^{\chi_1} U_{uq}^{\chi_2} \langle tu||rs \rangle^{\chi_3} + U_{tp}^{\chi_1} U_{ur}^{\chi_2} \langle tq||us \rangle^{\chi_3} + U_{tp}^{\chi_1} U_{us}^{\chi_2} \langle tq||ru \rangle^{\chi_3} \right. \\ &\quad \left. + U_{tq}^{\chi_1} U_{ur}^{\chi_2} \langle pt||us \rangle^{\chi_3} + U_{tq}^{\chi_1} U_{us}^{\chi_2} \langle pt||ru \rangle^{\chi_3} + U_{tr}^{\chi_1} U_{us}^{\chi_2} \langle pq||tu \rangle^{\chi_3}) \right] \\ &+ P_{123}^6 \left[\sum_{tuv} (U_{tp}^{\chi_1} U_{uq}^{\chi_2} U_{vr}^{\chi_3} \langle tu||vs \rangle + U_{tp}^{\chi_1} U_{uq}^{\chi_2} U_{vs}^{\chi_3} \langle tu||rv \rangle \right. \\ &\quad \left. + U_{tp}^{\chi_1} U_{ur}^{\chi_2} U_{vs}^{\chi_3} \langle tq||uv \rangle + U_{tq}^{\chi_1} U_{ur}^{\chi_2} U_{vs}^{\chi_3} \langle pt||uv \rangle) \right], \end{aligned} \quad (20)$$

while the derivatives of the overlap matrix are given as

$$\begin{aligned} \left(\frac{\partial^2 S_{pq}}{\partial \chi_1 \partial \chi_2}\right)^{(1)} &= S_{pq}^{\chi_1 \chi_2} + P_{12} \left[\sum_r (U_{rq}^{\chi_1} S_{pr}^{\chi_2} + U_{rp}^{\chi_1} S_{rq}^{\chi_2}) + \sum_r U_{rp}^{\chi_1} U_{rq}^{\chi_2} \right], \end{aligned} \quad (21)$$

$$\begin{aligned} \left(\frac{\partial^3 S_{pq}}{\partial \chi_1 \partial \chi_2 \partial \chi_3}\right)^{(1)} &= S_{pq}^{\chi_1 \chi_2 \chi_3} + P_{123}^3 \sum_r (U_{rq}^{\chi_1} S_{pr}^{\chi_2 \chi_3} + U_{rp}^{\chi_1} S_{rq}^{\chi_2 \chi_3}) \\ &+ P_{123}^6 \sum_{rs} U_{rp}^{\chi_1} U_{sq}^{\chi_2} S_{rs}^{\chi_3}, \end{aligned} \quad (22)$$

where quantities labeled by superscript χ_i again refer to derivatives of AO integrals rotated into the MO basis.

All equations presented so far hold for arbitrary CC schemes as well as MP2 theory. Furthermore, no assumptions have been made about the perturbations χ_1 , χ_2 , and χ_3 except for the fact that the wave function is assumed to remain real-valued under their influence. Accordingly, Eqs. (17)–(22) have to be modified if, for example, magnetic perturbations are studied.⁶² When considering the dipole Hessian matrix $d^3 E/dx dy d\epsilon$ with x and y as nuclear displacements and ϵ as a component of an external electric field, some simplifica-

tions arise from the fact that the derivatives of the AO two-electron integrals and overlap matrices with respect to ϵ vanish. We note that our expressions are not identical to those presented in Ref. 29 for the polarizability gradient $d^3 E/dx d\epsilon_i d\epsilon_j$, because in the latter article orbital relaxation was considered only for the geometrical perturbation x but not for the electric-field perturbations ϵ_i and ϵ_j . It is, however, possible to recover the expressions for orbital-unrelaxed derivatives by setting to zero the corresponding CPHF contributions in Eqs. (17)–(22). For hyperpolarizabilities and polarizability gradients, the equations for orbital-unrelaxed derivatives can be additionally modified to include a frequency dependence of the electric field.

III. IMPLEMENTATION

Based on the expressions presented in Section II, analytic dipole Hessians at the CCSD and MP2 levels of theory for use with closed-shell reference wave functions have been implemented into the quantum-chemical program package CFOUR.⁶³ Our implementation builds upon the preceding third-derivative scheme for polarizability gradients²⁹ and the general framework for analytic second derivatives available in CFOUR.²⁰ Since the latter is based on an asymmetric formulation, i.e., it already provides the solution of both

the first-order CC and Λ equations, no additional equations have to be solved for analytic third derivatives. However, in contrast to second derivatives, where a sequential treatment is possible, perturbed wave-function parameters corresponding to different perturbations are needed simultaneously for the construction of the second and third derivatives of the density matrices.

In our implementation, we first compute the first-order CC and Λ amplitudes as well as the first-order Z-vectors for all electrical perturbations and store them on disk. The first-order equations for the geometrical perturbations are then treated sequentially, while the final contributions to the dipole Hessian matrix are evaluated in a triangular fashion, i.e., once the amplitudes dt/dx and $d\lambda/dx$ have been calculated, the contributions to all elements $d^3E/dx dy d\epsilon$ with $x \geq y$ are formed. All expressions that involve second or third derivatives of AO integrals are evaluated in the AO basis after back-transformation of the perturbed and unperturbed one-particle and two-particle density matrices. The CPHF contributions to the higher-order derivatives of the Fock matrix, the overlap matrix, and the two-electron integrals are calculated according to Eq. (12), but we note that an evaluation where all CPHF terms are added to the corresponding density matrix prior to contraction with the integrals will most likely be advantageous in terms of computational time. However, such a reformulation is beyond the scope of the present article. Also, we note that our current implementation is not optimized with respect to memory requirements and it does not make use of point-group symmetry. Finally, we note that the computation of the dipole Hessian matrix requires no further integral derivatives than those needed for the calculation of the harmonic force constants apart from the second geometrical derivatives of the dipole integrals, which have been made available by interfacing the integral-derivative library GENINT⁶⁴ to CFOUR.

IV. PILOT APPLICATIONS

In this section, we illustrate the usefulness of analytic third derivatives by showing their superior accuracy as compared to numerical differentiation. For this purpose, we report the results of two series of calculations carried out with our new implementation: (1) An investigation of the higher-order geometrical derivatives of the dipole moment of hydrogen fluoride and (2) a study on the contribution to the dipole moment of hydrogen sulfide due to vibrational averaging.

A. Geometrical derivatives of the dipole moment of hydrogen fluoride

Table I summarizes the values for the geometrical derivatives $(d^n \mu_z / dR^n)_{R=R_{\text{eq}}}$ ($n = 1-4$, z -axis = molecular axis, $R_{\text{eq}} = 1.735686661$ a.u.) of the dipole moment of hydrogen fluoride as calculated at the CCSD level of theory using the cc-pCVDZ basis set.⁶⁵ The derivatives have been determined in three different manners, i.e., starting from the analytically evaluated dipole moment μ_z , from the dipole gradient $d\mu_z/dR$, and from the dipole Hessian $d^2\mu_z/dR^2$. The remaining differentiation steps were carried out numerically using the formulas

$$\left(\frac{dA}{dR}\right)_{R=R_{\text{eq}}} = \frac{A(R_{\text{eq}} + \Delta R) - A(R_{\text{eq}} - \Delta R)}{2\Delta R}, \quad (23)$$

$$\begin{aligned} \left(\frac{d^2A}{dR^2}\right)_{R=R_{\text{eq}}} &= \frac{A(R_{\text{eq}} + \Delta R) - 2A(R_{\text{eq}}) + A(R_{\text{eq}} - \Delta R)}{\Delta R^2}, \quad (24) \end{aligned}$$

$$\left(\frac{d^3A}{dR^3}\right)_{R=R_{\text{eq}}} = \frac{A(R_{\text{eq}} + 2\Delta R) - 2A(R_{\text{eq}} + \Delta R) + 2A(R_{\text{eq}} - \Delta R) - A(R_{\text{eq}} - 2\Delta R)}{2\Delta R^3} \quad (25)$$

with A denoting the analytically evaluated quantity. In all calculations, convergence criteria were chosen such that the energy was determined to a precision of 13 decimal places. It is not straightforward to deduce the accuracy of the analytically calculated dipole moment, dipole gradient, and dipole Hessian from the accuracy of the energy, but as a conservative estimate we assume a precision of 12 decimal places in the following.

The results in Table I show how repeated numerical differentiation impairs the accuracy of a target quantity and the impact of both errors discussed in Section I is clearly visible. On the one hand, the number of significant digits in the values for the numerical derivatives inevitably shrinks when using small step sizes ΔR or seeking higher derivatives. On

the other hand, values obtained with large step sizes ΔR are significantly contaminated by higher derivatives and thus inaccurate. By means of error propagation, the error due to the uncertainty η in the undifferentiated quantity can be estimated as $\eta/\Delta R^n$, while the error due to discretization is always proportional to ΔR^2 . From this, it follows that the overall error is minimized when using a step size of $\Delta R = \sqrt[n+2]{\eta}$, i.e., for the present example ($\eta = 10^{-12}$) $\Delta R \approx 10^{-4}$ for a single differentiation step, $\Delta R \approx 10^{-3}$ for two differentiation steps, and $\Delta R \approx 10^{-2}$ for three differentiation steps. The values in Table I confirm these estimates and the comparison to the fully analytical values for $d\mu_z/dR$ and $d^2\mu_z/dR^2$ shows that seven and five significant digits are within reach when differentiating numerically once and twice, respectively. When considering

TABLE I. Geometrical derivatives of the dipole moment of hydrogen fluoride at the CCSD/cc-pCVDZ level of theory in atomic units, bond lengths optimized at the same level of theory ($R_{\text{eq}} = 1.735686661$ a.u.).

Computed from	$\Delta R/\text{\AA}$	$\left(\frac{d\mu_z}{dR}\right)_{R=R_{\text{eq}}}$	$\left(\frac{d^2\mu_z}{dR^2}\right)_{R=R_{\text{eq}}}$	$\left(\frac{d^3\mu_z}{dR^3}\right)_{R=R_{\text{eq}}}$	$\left(\frac{d^4\mu_z}{dR^4}\right)_{R=R_{\text{eq}}}$	$\left(\frac{d^5\mu_z}{dR^5}\right)_{R=R_{\text{eq}}}$
μ_z	10^{-2}	-0.3173676440	0.17871386	0.763567	0.0750	...
μ_z	10^{-3}	-0.317412644	0.178712	0.764
μ_z	10^{-4}	-0.31741309	0.1787
μ_z	10^{-5}	-0.3174131	0.18
$d\mu_z/dR$	10^{-2}	...	0.1787160589	0.76369291	0.0748442	2.112
$d\mu_z/dR$	10^{-3}	...	0.178711645	0.763745	0.0714	...
$d\mu_z/dR$	10^{-4}	...	0.17871157	0.7656
$d\mu_z/dR$	10^{-5}	...	0.1787139	0.77
$d^2\mu_z/dR^2$	10^{-2}	0.7636297628	0.075009981	2.11131
$d^2\mu_z/dR^2$	10^{-3}	0.763754290	0.0750835	2.11
$d^2\mu_z/dR^2$	10^{-4}	0.76375554	0.07509	...
$d^2\mu_z/dR^2$	10^{-5}	0.7637555	0.075	...
Fully analytical value		-0.31741303392	0.17871155406

these numbers, one should bear in mind that a precision of 13 decimal places in the value for the energy is often not achievable when studying larger molecules or employing larger basis sets. The accuracy obtained here should thus be regarded as an upper bound. Since five significant decimal places is already less than what is sometimes required in quantum-chemical applications, one can conclude from the present example that at most two differentiation steps should be carried out numerically. We note that the performance of numerical differentiation can be improved by taking into consideration more points, but such protocols entail higher computational cost. This shows that the reliable calculation of higher derivatives is greatly facilitated when starting from analytic third derivatives as they can be determined with guaranteed precision. At the same time, our results also provide a justification for current efforts^{49,66} to implement even higher than third-order analytic derivatives.

B. Vibrationally averaged dipole moment of hydrogen sulfide

Within the harmonic approximation, the expectation value for a generic molecular property A can be expanded in the normal-coordinate space as^{56,67}

$$\langle A \rangle = A_e + \sum_i \frac{dA}{dq_i} \langle q_i \rangle + \frac{1}{2} \sum_i \frac{d^2A}{dq_i^2} \langle q_i^2 \rangle + \dots, \quad (26)$$

where A_e stands for the equilibrium contribution and the remaining terms represent the contributions from vibrational averaging. The latter involve the first and second property derivatives dA/dq_i and d^2A/dq_i^2 as computed at the equilibrium structure as well as the expectation values of the normal coordinates q_i and their squares q_i^2 , which are given as

$$\langle q_i \rangle = -\frac{1}{4\omega_i^2} \sum_j \frac{\phi_{ijj}}{\omega_j}, \quad (27)$$

$$\langle q_i^2 \rangle = \frac{1}{2\omega_i} \quad (28)$$

with ω_i denoting the harmonic force constants and ϕ_{ijj} the semidiagonal cubic force constants in terms of normal coordinates.

The determination of vibrationally averaged properties in a black-box manner is desirable. The common practice^{56,67} has, however, been to evaluate the higher-order quantities involved in Eqs. (26)–(28), i.e., d^2A/dq_i^2 and ϕ_{ijj} by numerical differentiation, which in some cases renders the reliable determination of the vibrational averaging contributions cumbersome and results questionable. With our new implementation for the dipole Hessian matrix, the fully analytic evaluation of the third term in Eq. (26) becomes possible for vibrationally averaged dipole moments. To demonstrate how analytic third derivatives can help to increase the reliability and robustness of the calculation of vibrationally averaged properties, we have studied the contributions from vibrational averaging to the dipole moment of hydrogen sulfide at the MP2 and CCSD levels of theory using the aug-cc-pCVXZ ($X = D, T, Q$) basis sets.^{65,68,69} The results are reported in Table II. All calculations were carried out after optimizing the molecular structure at the corresponding level of theory and performed three times starting from either analytic first, second, or third derivatives. Also, two different sets of convergence criteria were used in all calculations: One denoted as tight, where we chose all convergence thresholds as tight as possible and one denoted as loose, where we applied modest criteria for all relevant equations, which is generally not recommendable but not always avoidable and thus a better estimate for application-level calculations. Details are given in Table II.

Several conclusions can be drawn from our results. First, it is seen that the sensitivity towards the choice of convergence criteria grows as expected with the number of differentiation steps that are carried out numerically. The fully analytic evaluation yields acceptable results for all cases considered here, whereas for double numerical differentiation this is the case only when using tight convergence thresholds. In contrast, the combination of loose convergence thresholds and double numerical differentiation may lead to unreliable results. Also, all CCSD results show a greater sensitivity towards the

TABLE II. Contributions from $d^2\mu/dq_i^2$ to the vibrationally averaged dipole moment of hydrogen sulfide at the MP2 and CCSD levels of theory using the aug-cc-pCVXZ ($X = D, T, Q$) basis sets, structures optimized at the corresponding levels of theory. All values in atomic units.

Computed from	Convergence criteria ^a	MP2			CCSD	
		aug-cc-pCVDZ	aug-cc-pCVTZ	aug-cc-pCVQZ	aug-cc-pCVDZ	aug-cc-pCVTZ
Analytic 1st derivatives	Tight	-0.00095130	-0.00104688	-0.00117564	-0.00005073	-0.00002575
	Loose	-0.00089444	-0.00103934	-0.00116499	0.00000556	-0.00002076
Analytic 2nd derivatives	Tight	-0.00095131	-0.00104688	-0.00117565	-0.00005073	-0.00002575
	Loose	-0.00095123	-0.00104705	-0.00117588	-0.00005395	-0.00002682
Analytic 3rd derivatives	Tight	-0.00095137	-0.00104682	-0.00117562	-0.00005079	-0.00002570
	Loose	-0.00095138	-0.00104683	-0.00117565	-0.00005032	-0.00002605
Total dipole moment (μ)		-0.41640541	-0.38849189	-0.39125213	-0.40316564	-0.38499795

^aThe HF-SCF equations were considered converged when the maximum absolute change in the density-matrix elements fell below a value of 10^{-N} a.u. The zeroth-order and first-order CC and Λ equations were considered converged when the maximum absolute change in the amplitudes fell below a value of 10^{-N} a.u. Tight thresholds: $N = 11$ for the aug-cc-pCVDZ basis set and $N = 10$ for the aug-cc-pCVTZ and the aug-cc-pCVQZ basis set. Loose thresholds: $N = 6$ for all basis sets.

convergence thresholds than the corresponding MP2 results, which is due to the fact that for a CCSD calculation more equations need to be solved than for an MP2 calculation: The calculation of the first energy derivative requires the solution of the HF-SCF and the Z-vector equations at the MP2 level of theory, while for CCSD one needs to solve for the CC and Λ amplitudes as well. Likewise, calculating the second and third energy derivative involves in addition to a gradient calculation the solution of the first-order Z-vector equations for MP2, but also the solution of the first-order CC and Λ equations for CCSD. For the molecule studied here, these factors lead to inaccurate results especially for the CCSD/aug-pCVDZ calculation, where loose convergence criteria and double numerical differentiation were applied. We note that this example is not artificial, rather it is representative of routinely performed vibrational averaging calculations.⁷⁰

To investigate the problems with this calculation in further detail, we have summarized in Table III the contributions from individual normal coordinates to the values from Table II. This shows that the contributions from the bending mode and the symmetric stretch mode vary in the sixth decimal place at most, while those from the asymmetric stretch mode differ already in the fifth decimal place. For the latter mode, acceptable accuracy in combination with loose convergence criteria is achieved only when using analytic third derivatives. We add that such problematic normal coordinates

cannot be easily identified. In total, this clearly shows that a black-box evaluation of the vibrational averaging contribution is only possible when using analytic third derivatives.

V. CONCLUDING REMARKS

In this article, we have presented the derivation of a generic analytical expression for the third derivative of the CC energy together with an implementation of the dipole Hessian matrix at the MP2 and CCSD levels of theory and some pilot applications. In contrast to preceding work on analytic third derivatives in CC theory,^{23–25,29} our implementation considers for the first time orbital relaxation for all perturbations. Our work should thus be seen as a key step towards the fully analytical evaluation of anharmonic effects at CC levels of theory. A number of extensions of our current implementation are worthwhile to pursue and will help make analytic third derivatives a standard tool in CC theory as analytic first and second derivatives already are: The implementation of cubic force constants at the MP2 and CCSD levels of theory is currently under way. Put together with the present code for the dipole Hessian matrix, this will facilitate the thorough investigation of anharmonic effects in vibrational spectra at correlated levels of theory. Furthermore, we aim at extending our implementation to other third-order properties. Specifically, the availability of gradients for second-order properties

TABLE III. Contributions from $d^2\mu/dq_i^2$ to the vibrationally averaged dipole moment of hydrogen sulfide at the MP2 and CCSD levels of theory using the aug-cc-pCVDZ basis set broken down to individual normal coordinates, structures optimized at the corresponding levels of theory. All values are in atomic units.

Computed from	Convergence criteria ^a	Bending		Symmetric stretch		Asymmetric stretch	
		MP2	CCSD	MP2	CCSD	MP2	CCSD
Analytic 1st derivatives	Tight	-0.00100065	-0.00079515	0.00034601	0.00062513	-0.00029666	0.00011929
	Loose	-0.00100054	-0.00079410	0.00034583	0.00062423	-0.00023974	0.00017543
Analytic 2nd derivatives	Tight	-0.00100065	-0.00079515	0.00034601	0.00062513	-0.00029666	0.00011929
	Loose	-0.00100068	-0.00079579	0.00034601	0.00062479	-0.00029656	0.00011704
Analytic 3rd derivatives	Tight	-0.00100074	-0.00079524	0.00034602	0.00062514	-0.00029665	0.00011931
	Loose	-0.00100076	-0.00079520	0.00034602	0.00062512	-0.00029665	0.00011994

^aSee footnote to Table II for explanation.

and Hessian matrices for first-order properties will allow for a more reliable evaluation of vibrational averaging contributions to the corresponding properties than is possible with current schemes. Finally, a generalization of our CCSD implementation to arbitrary CC schemes and there in particular the CCSD(T) approach is desirable in order to investigate the impact of higher excitations on anharmonic effects.

ACKNOWLEDGMENTS

The authors thank Magnus Ringholm and Bin Gao for helpful discussions. T.-C. Jagau has been supported by the graduate school “Materials Science in Mainz.” This work has been funded in Germany by the Deutsche Forschungsgemeinschaft (Grant No. GA 370/5-1) and the Fonds der chemischen Industrie and in Norway by the Centre for Theoretical and Computational Chemistry (Grant No. 179568/V30).

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