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## ▶ To cite this version:

Jürgen Gauss, Mihaly Kallay, Darragh P. O'Neill. Analytic evaluation of Raman intensities in coupled-cluster theory. Molecular Physics, 2008, 105 (19-22), pp.2447-2453. 10.1080/00268970701516412 . hal-00513122

## HAL Id: hal-00513122 https://hal.science/hal-00513122

Submitted on 1 Sep 2010

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#### **Molecular Physics**



# Analytic evaluation of Raman intensities in coupled-cluster theory

Journal:	Molecular Physics		
Manuscript ID:	TMPH-2007-0143.R1		
Manuscript Type:	Full Paper		
Date Submitted by the Author:	10-Jun-2007		
Complete List of Authors:	Gauss, Jürgen; Universität Mainz, Institut für Physikalische Chemie Kallay, Mihaly; Budapest University of Technology and Economics, Department of Physical Chemistry O'Neill, Darragh; Universität Mainz, Institut für Physikalische Chemie		
Keywords:	coupled-cluster theory, analytic third derivatives, polarizability derivatives, Raman spectroscopy		
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.			

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Molecular Physics, Vol. 00, No. 00, DD Month 200x, 1-10

### Analytic evaluation of Raman intensities in coupled-cluster theory

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(Received 00 Month 200x; in final form 00 Month 200x)

We present the first implementation for the analytic calculation of polarizability derivatives using coupled-cluster theory. These derivatives are related to the intensity of bands seen in Raman spectroscopy, and are therefore important quantities which can also be measured experimentally. The required theory of analytic third derivatives is discussed and also connected to response theory to allow the calculation of frequency-dependent quantities. This work includes the use of a string-based general coupled-cluster/configuration-interaction program which makes the calculation of Raman intensities for arbitrary coupled-cluster or configurationinteraction methods up to the full configuration interaction limit possible. Some demonstrative examples are given, with some investigation into the importance of higher-order excitations in the theoretical predictions of Raman intensities.

*Keywords:* Coupled-cluster theory, analytic third derivatives, Raman spectroscopy, polarizability derivatives

#### 1 Introduction

Molecules are usually characterized via their geometrical structure, whose computational determination requires the evaluation of the forces on the nuclei. To efficiently determine them analytic differentiation techniques are used, the first implementation of which was reported in 1969 by Pulay [1] for Hartree-Fock selfconsistent-field (HF-SCF) wavefunctions. This pivotal work on HF-SCF energy gradients was soon extended to both higher derivatives of the energy, as well as to derivatives for electron-correlated approaches (for reviews on these topics see Refs. [2–4]). In particular, the implementation for analytic second [5–9] and third derivatives [10–13] enabled the efficient evaluation of vibrational frequencies and infrared intensities within the harmonic approximation, of anharmonic force constants, and of Raman intensities. After almost 40 years the field of analytic derivatives continues to grow, allowing the evaluation of more properties for more accurate quantum-chemical models (see, for example, Refs. [14, 15]). In this work, analytic third derivatives of the energy will be reported for the evaluation of Raman intensities using coupled-cluster (CC) and configuration-interaction (CI) methods.

Fully analytic techniques for the evaluation of Raman intensities requiring geometrical derivatives of the polarizability tensor have, so far, only been implemented at the HF-SCF level [16, 17], while corresponding electron-correlated calculations have relied on finite-difference schemes [18–22]. This usually involves numerically differentiating analytically evaluated polarizabilities with respect to the nuclear coordinates. Such schemes have been applied at the coupled-cluster level using the CC

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ISSN 00268976 print/ISSN 13623028 online © 200x Taylor & Francis http://www.tandf.co.uk/journals DOI: 10.1080/0026897YYxxxxxxx

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singles and doubles (CCSD) [23], as well as the CC3 approximation [24], the latter including an approximate treatment of triple excitations. Using CC response theory to evaluate the frequency-dependent polarizability [25,26], it has, in addition, been possible to investigate the frequency-dependence of Raman intensities [19–22].

In this work, we will present for the first time a fully analytic scheme for the evaluation of Raman intensities at the CC level and will investigate electroncorrelation effects on Raman intensities using a hierarchy of CC methods up to the full configuration-interaction (FCI) limit. We will first describe the relevant quantities required for the calculation of Raman intensities, followed by a brief discussion of analytic third derivatives within CC theory, necessary for the evaluation of the required polarizability derivatives. To compute frequency-dependent Raman intensities, the close relationship between analytic derivatives and response theory is invoked [14]. Implementation will be reported for the CCSD model (within the quantum-chemical program package ACESII (Mainz-Austin-Budapest version) [27]) and for arbitrary CC models including higher excitations, i.e., CC singles, doubles, triples (CCSDT), CC singles, doubles, triples, quadruples (CCSDTQ), ... up to FCI, using string-based many-body techniques [28, 29] as they have been used in the general CC/CI package MRCC [30]. To investigate the effect of higher excitations on computed Raman intensities, test calculations are reported for a series of small molecules (BH, HF,  $H_2O$ , and  $N_2$ ).

#### 2 Theory

Within the harmonic approximation and Placzek's polarizability theory [31], Raman intensities are related to the geometric derivative of the polarizability tensor. In this study the system-inherent Raman activity I and the decoherence ratio  $\rho$ are the quantities on which we shall focus and which, for a particular normal mode Q, are defined as

$$I = 45\alpha'^2 + 7\gamma'^2 \tag{1}$$

and

$$\rho = \frac{3{\gamma'}^2}{45{\alpha'}^2 + 4{\gamma'}^2}.$$
 (2)

In Eqs. (1) and (2) the derivatives of the isotropic polarizability  $\alpha$  and the anisotropic polarizability  $\gamma$  are given by

$$\alpha' = \frac{1}{3} \left\{ \bar{\alpha}'_{xx} + \bar{\alpha}'_{yy} + \bar{\alpha}'_{zz} \right\}$$
(3)

$$(\gamma')^{2} = \frac{1}{2} \left\{ \left[ \bar{\alpha}'_{xx} - \bar{\alpha}'_{yy} \right]^{2} + \left[ \bar{\alpha}'_{xx} - \bar{\alpha}'_{yy} \right]^{2} + \left[ \bar{\alpha}'_{xx} - \bar{\alpha}'_{yy} \right]^{2} + 6 \left[ \bar{\alpha}'_{xy}^{2} + \bar{\alpha}'_{yz}^{2} + \bar{\alpha}'_{zx}^{2} \right] \right\}$$

$$(4)$$

where the derivative of the polarizability tensor with respect to Q is given by

$$\bar{\alpha}_{ij}' = \frac{\partial \alpha_{ij}}{\partial Q} \tag{5}$$

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and  $\alpha_{ij}$  are the elements of the Cartesian polarizability tensor.

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Considering first the frequency-independent (static) Raman intensities, the corresponding polarizability derivatives are given by the following third derivatives of the energy E

$$\alpha_{ij}' = \frac{\mathrm{d}^3 E}{\mathrm{d} x_i \mathrm{d} \varepsilon_i \mathrm{d} \varepsilon_j} \tag{6}$$

where  $x_i$  denotes the Cartesian coordinate of one of the nuclei and  $\varepsilon_p, p = x, y, z$ are the electric-field components.

Within CC theory, expressions for the third derivative in Eq. (6) can be obtained by replacing the energy E by the following energy functional [32, 33]

$$\tilde{E} = \langle 0|(1+\Lambda)\exp(-T)H\exp(T)|0\rangle$$
(7)

which can be made stationary with respect to both the cluster amplitudes  $t_p$  in the cluster operator T and the Lagrange multipliers  $\lambda_p$  which constitute the socalled  $\Lambda$  operator. In this way, it is possible to exploit the usual (2n + 1) [11] and (2n+2) rules [32] and to derive expressions for the third derivatives of the energy which contain at most first derivatives of the wavefunction parameters. This Lagrangian formulation efficiently deals with the non-variational nature of the coupled-cluster energy, but another important issue in analytic derivative theory is that of the response of the reference determinant to the perturbation, known as orbital relaxation. The functional, Eq. (7), can thus be augmented to yield the following

$$\tilde{E} = \langle 0|(1+\Lambda)\exp(-T)H\exp(T)|0\rangle + \sum_{ai} Z_{ai}f_ai + \sum_{pq} I_{pq}(S_{pq} - \delta_{pq})$$
(8)

where the last two terms represent the Brillouin and the orthonormality conditions for the molecular orbitals (MO), and the Lagrangian multipliers  $Z_{ai}$  and  $I_{pq}$  are otherwise known as the Z-vector [34] and the energy-weighted density matrix,  $\delta_{pq}$ is the Kronecker delta symbol, and  $f_{pq}$  and  $S_{pq}$  are the usual Fock and overlap integrals. Throughout this work the indices  $i, j, \ldots$  refer to occupied orbitals,  $a, b, \ldots$ to virtual orbitals and  $p, q, \ldots$  to all orbitals.

To evaluate frequency-dependent (dynamic) Raman intensities, the frequencydependent polarizability must be considered in Eqs. (1) to (6), whose evaluation is possible using response theory [35]. The close relationship between linear response theory and analytic second derivatives has already been used to evaluate frequency-dependent polarizabilities [14], and this can be extended in a straightforward manner to write down the derivative of the frequency-dependent polarizability with respect to the nuclear coordinates

$$\alpha_{ij}'(\omega) = \frac{1}{2} C^{\pm \omega} \frac{\mathrm{d}^3 \{L_{CC}\}_T}{\mathrm{d}x_i \mathrm{d}\varepsilon_i \mathrm{d}\varepsilon_j}; \qquad \omega = \omega_j = -\omega_i \tag{9}$$

where  $\{L_{CC}\}_T$  is the time-averaged quasi-energy Lagrangian [35]. The symmetrization operator  $C^{\pm\omega}$ , which reverses the sign of all frequencies, ensures that only the real part of the response function is considered. The parametric dependence of the frequencies  $\omega_i = -\omega_i$  is a result of the time averaging, which only yields a nonvanishing result when the sum of all frequencies is zero. The practical implication of this reformulation is that the perturbed amplitude and  $\Lambda$  equations must be solved with the inclusion of a frequency-dependent term as described in Ref. [14].

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In the discussion of analytic derivative techniques above, the issue of orbital relaxation was mentioned. In the case of frequency-dependent properties this must be applied with caution as it can lead to unphysical results [35]. The response function contains poles at certain frequencies corresponding to electronic excitations in the coupled-cluster wavefunction, but if the reference determinant is also allowed to respond to the perturbation, an additional unphysical set of poles will be introduced into the response function. To avoid such problems we do not include orbital relaxation with respect to frequency-dependent properties. It is noted that in the case of static electrical properties, it has been shown that the inclusion of orbital relaxation effects does not necessarily provide superior results [36] and that in fact CC theory implicitly includes some of these effects through the single excitation operator [37]. In the case of geometric parameters, it is necessary to include orbital relaxation, and hence in this work the reference determinant is allowed to respond only to the geometric perturbation, but not the two electrical perturbations.

Starting from the coupled-cluster energy Lagrangian in Eq. (8) we differentiate three times in total, once with respect to a nuclear coordinate x and twice with respect to the electric field components  $\varepsilon_i$  and  $\varepsilon_j$ , to yield the following expression

$$\begin{aligned} \alpha_{ij}'(\omega) &= \frac{1}{2} C^{\pm \omega} \Big\{ P(i,j) \sum_{pq} \left( \frac{\partial D_{pq}}{\partial \varepsilon_i} \right)^{(1,1)} \left( \frac{\partial^2 f_{pq}}{\partial \varepsilon_j \partial x} \right)^{(1)} \\ &+ \sum_{pq} \left( \frac{\partial^2 D_{pq}}{\partial \varepsilon_i \partial \varepsilon_j} \right)^{(1,1)} \frac{\partial f_{pq}}{\partial x} + P(i,j) \sum_{pq} \left( \frac{\partial^2 D_{pq}}{\partial x \partial \varepsilon_j} \right)^{(1,1)} \frac{\partial f_{pq}}{\partial \varepsilon_i} \\ &+ \sum_{pqrs} \left( \frac{\partial^2 \Gamma_{pqrs}}{\partial \varepsilon_i \partial \varepsilon_j} \right)^{(1,1)} \frac{\partial \langle pq || rs \rangle}{\partial x} + \sum_{pqrs} \left( \frac{\partial^3 \Gamma_{pqrs}}{\partial x \partial \varepsilon_i \partial \varepsilon_j} \right)^{(1,1)} \langle pq || rs \rangle \Big\} \end{aligned}$$
(10)

where  $D_{pq}$  and  $\Gamma_{pqrs}$  are the effective one- and two-particle density matrices,  $\langle pq | | rs \rangle$  are the anti-symmetrized two-electron integrals and P(i, j) permutes the indices *i* and *j*. We have used the (2n+1) rule for wavefunction parameters (cluster amplitudes and MO coefficients) and the (2n+2) rule for Lagrangian multipliers ( $\Lambda$  amplitudes, *Z*-vector and energy-weighted density matrix), and to exploit this efficiently we have introduced the notation

$$\left(\frac{\partial^n A}{\partial \alpha \partial \beta \dots}\right)^{(k_T,k_\Lambda)}$$
 and  $\left(\frac{\partial^n I}{\partial \alpha \partial \beta \dots}\right)^{(k)}$ , (11)

subeqn.sty which indicates that the *n*th derivative of the density matrix A contains at most the  $k_T$ th and  $k_{\Lambda}$ th derivatives of the T and  $\Lambda$  amplitudes, and that the *n*th derivative of the integral I contains at most kth order coupled-perturbed Hartree-Fock (CPHF) coefficients. For example the second derivative of the Fock matrix in Eq. (10) is defined by

$$\left(\frac{\partial^2 f_{pq}}{\partial x \partial \varepsilon_j}\right)^{(1)} = \langle p|\mu_j|r\rangle U_{rq}^x + U_{rp}^x \langle r|\mu_j|q\rangle + \sum_{\nu} \left(c_{\nu p} \langle \frac{\partial \nu}{\partial q_i} |\mu_j|q\rangle + \langle p|\mu_j| \frac{\partial \nu}{\partial q_i} \rangle c_{\nu q}\right)$$
(12)

where  $\mu_j$  is the electric-dipole operator,  $U_{pq}^x$  are the CPHF coefficients corresponding to perturbation x,  $c_{\nu i}$  are the MO coefficients and  $\nu$  are the atomic orbitals.

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Due to the (2n + 1) rule, the second derivative of  $f_{pq}$  in Eq. (10) contains no second-order CPHF coefficients.

Expressions for the effective density matrices for different quantum-chemical methods can be found in the literature [38–41]. In the frequency-dependent case, the perturbed T and  $\Lambda$  amplitudes used to construct these density matrices are evaluated by solving the corresponding response equations, which includes a frequency-dependent contribution, and this has been described in detail in Ref. [14].

#### 3 Implementation

The required third-derivative framework for the calculation of Raman intensities has been built upon the existing second-derivative scheme [8] available in the Mainz-Austin-Budapest version of ACESII [27]. This is particularly convenient as the asymmetric implementation [8,42], which does not adhere to the (2n+1) and (2n+2) rules, requires the solution of both the perturbed first-order amplitude and first-order  $\Lambda$  equations. No further perturbed wavefunction parameter is required for third-derivatives. However, whereas in the case of analytic second-derivatives where perturbed quantities are required only one perturbation at a time, allowing them to be evaluated sequentially, in the case of third derivatives all perturbed wavefunction parameters are needed simultaneously for the evaluation of secondand third-order perturbed density matrices. For Raman intensities, in particular, the perturbed amplitude and  $\Lambda$  equations are first solved for all electrical perturbations (and frequencies in the frequency-dependent case) and the perturbed T and  $\Lambda$  amplitudes are then stored to disk. The geometrical perturbations can then be treated sequentially, i.e., for each geometrical perturbation the perturbed equations are solved, the required perturbed density matrices are evaluated and contracted 'on the fly' with the corresponding integrals, after which the perturbed T and  $\Lambda$ amplitudes for this perturbation are no longer needed.

This scheme requires the storage of wavefunction parameters for all electrical perturbations, and in principle for a full third derivative calculation the storage of parameters for all perturbations would be required. Concerns about the required amount of disk space are justified, but we take the pragmatic approach, that an implementation which avoids this, if even possible, would require an unjustifiable amount of time to implement. Furthermore, such high accuracy calculations are limited to small systems and hence for the size of system which can be considered, the disk space requirements are not unreasonable in terms of that available on modern computers.

In order to include higher than double excitations in the CC expansion, we have interfaced the third-derivative scheme in ACESII with the general-CC code MRCC [30]. In MRCC a string-based algorithm is exploited to provide an efficient implementation of CC and CI models up to arbitrary levels of excitation [28,29]. This scheme has already been extended to provide first [43] and second derivatives [9] of coupled-cluster energies including arbitrary excitations and more recently has been combined with response theory to calculate frequency-dependent polarizabilities [14] and frequency-dependent hyperpolarizabilities [15]. In this work, the program package MRCC is used to solve all amplitude and  $\Lambda$  equations and also to compute all required density matrices and thus allows, when interfaced with ACE-SII, the calculation of Raman intensities for CCSD, CCSDT, CCSDTQ, etc., as well as the corresponding configuration-interaction (CI) methods CISD, CISDT, CISDTQ, etc. up to the FCI limit. We note that for all of the CI methods the last term in Eq. (10) may be ignored as the third derivative of the two-particle density matrix vanishes.

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#### 4 Applications

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We consider here some small systems to examine the importance of higher excitations in the theoretical prediction of Raman intensities. Due to the computational expense of some of these calculations, we have had to limit ourselves to small molecules using small basis sets. With the exception of BH, all calculations have been performed using the Sadlej basis set [44, 45], a medium sized basis set parametrized to reproduce polarizabilities, and which has been shown to provide results comparable to the larger aug-cc-pVTZ [46,47] basis when calculating Raman intensities, but at a much lower computational cost [19, 48]. For BH the smaller aug-cc-pVDZ [46, 47] basis set was used to facilitate the FCI calculations. Frequency-dependent Raman intensities are calculated at a wavelength of 514.5 nm ( $\omega = 0.088559$  a.u.), with the exception of BH. All calculations are performed at the equilibrium geometry for the given method and basis set. As we do not currently have an implementation of analytic Raman intensities using the CC3 method, all CC3 results given have been calculated by evaluating the polarizability derivatives by finite difference, using a stepsize of 0.001 a.u. [21]. This allows comparison with previous results of investigations on diatomic molecules including triple excitations [21]

#### 4.1 BH

BH is a sufficiently small molecule, such that FCI calculations are possible, although only for quite a modest basis set, namely aug-cc-pVDZ [46, 47]. Although  $\omega =$ 0.088559 a.u. ( $\lambda = 514.5$  nm) is a typical frequency, at which to evaluate dynamic Raman intensities, in the case of BH, using this basis set, we do not use this value, as there is a pole in the polarizability in this region ( $\omega_{\text{exc}} \approx 0.11$  a.u.) and Placzek's theory does not hold in this case. Instead we treat BH as a benchmark case and calculate for CCSD, CC3, CCSDT, CCSDTQ and FCI the Raman intensities at the frequencies  $\omega = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$  a.u. to examine the effects of higher excitations in the static and frequency-dependent cases.

The results for BH are summarized in Table 1. It is observed that in this case higher excitations do not play an important role in the prediction of Raman intensities, and that the CCSD values are within 1% of the FCI numbers, with the error increasing slowly with increasing frequency.

#### 4.2 HF

The results for the HF molecule are summarized in Table 2. Again we see similar results to those of BH, in that the inclusion of triples is not essential for a quantitative description of the Raman intensities, as has been noted before [20], and amounts to only  $\sim 1\%$ . Excellent agreement is seen between the CC3 and CCSDT models. For the chosen frequency, at least, the effect of triples is approximately equal in the static and dynamic cases.

#### 4.3 $H_2 O$

This work on  $H_2O$  is the first time, for Raman intensities, that triple excitations have been examined in molecules bigger than diatomics and the results are given in Table 3. Again it is observed that CCSD is seen to be performing well in the prediction of Raman intensities, with the values deviating from those of CCSDT by approximately 1%. The importance of triple excitations is more or less equal in

 Table 1. Static and dynamic Raman intensites I (Å<sup>4</sup>amu<sup>-1</sup>) and decoherence ratios  $\rho$  for BH obtained at various frequencies  $\omega$  (in a.u.) and at various coupled-cluster levels up to FCI using the aug-cc-pVDZ basis. All calculations have been performed at the corresponding equilibrium geometries, bond distances  $r_{\rm BH}$  (in a.u.) and harmonic vibrational frequencies  $\nu_1$  (in cm<sup>-1</sup>) are given as well

harmonic vibrational frequencies $\nu_1$ (in cm <sup>-1</sup> ) are given as well.					
	CCSD	CC3	CCSDT	CCSDTQ	FCI
$r_{\rm BH}$	2.36328	2.36540	2.36602	2.36602	2.36602
$ u_1$	2337.24	2328.17	2325.31	2325.42	2325.42
$\omega = 0.00$					
Ι	215.11	214.87	214.34	214.55	214.55
ho	0.56	0.56	0.55	0.55	0.55
$\omega = 0.01$					
Ι	216.09	215.82	215.28	215.49	215.49
ρ	0.57	0.56	0.56	0.55	0.55
$\omega = 0.02$					
Ι	219.17	218.81	218.24	218.43	218.43
$\rho$	0.58	0.57	0.57	0.57	0.57
$\omega = 0.03$					
Ι	224.86	224.33	223.68	223.85	223.85
ρ	0.60	0.59	0.59	0.59	0.59
$\omega = 0.04$					
Ι	234.27	233.44	232.65	232.78	232.78
ρ	0.63	0.63	0.62	0.62	0.62
$\omega = 0.05$					
Ι	249.84	248.47	247.46	247.51	247.51
ρ	0.68	0.67	0.67	0.66	0.66

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Table 2. Static and dynamic Raman intensities  $I(\text{Å}^4 \text{amu}^{-1})$  and decoherence ratios  $\rho$  for HF obtained at various coupled-cluster levels up to FCI using the Sadlej basis. All calculations have been performed at the corresponding equilibrium geometries, bond distances  $r_{\text{HF}}$  (in a.u.) and harmonic vibrational frequencies  $\nu_1$  (in cm<sup>-1</sup>) are given as well.

	CCSD	CC3	CCSDT	
$r_{ m HF}$	1.74850	1.75297	1.75236	
$ u_1 $	4113.60	4070.61	4076.22	
$\lambda = \infty$				
Ι	43.67	42.80	42.86	
ho	0.12	0.12	0.12	
$\lambda = 514.5~\mathrm{nm}$				
Ι	47.05	46.13	46.20	
ρ	0.12	0.12	0.12	

both the static and dynamic cases. Although it is possible to compare these values with experimental values in the literature [18], it has been shown previously [19–21] that such comparisons are not useful due to the experimental uncertainty and the approximations inherent to Placzek's theory.

#### 4.4 $N_2$

The static and dynamic Raman intensities for  $N_2$  as obtained at various levels of coupled-cluster theory are shown in Table 4. In contrast to the previous examples, the inclusion of triple excitations is essential in this case, with the deviations from the CCSD results amounting to approximately 30% for CC3 and almost 20% for CCSDT. Since the polarizability does not show such a strong variation with increasing levels of theory [36], a similar trend might have been also expected for their derivative. However, the rather large change of the

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Table 3. Static and dynamic Raman intensites I (Å<sup>4</sup>amu<sup>-1</sup>) and decoherence ratios  $\rho$  for H<sub>2</sub>O obtained at various coupled-cluster levels up to FCI using the Sadlej basis. All calculations have been performed at the corresponding equilibrium geometries, bond distances  $r_{\rm OH}$  (in a.u.), bond angles  $\angle$ HOH (in degrees) and harmonic vibrational frequencies  $\mu_i$  (in cm<sup>-1</sup>) are given as well

$\nu_i$ (in cm ) are given				as wen.		
	CCS	CCSD		TC		
$r_{\rm OH}$	1.827	1.82780		1.83177		
∠HOH	103.8	103.83		103.63		
$\nu_1$	3814.	3814.82		3780.52		
$\nu_2$	1669.	1669.61		1659.34		
$\nu_3$	3933.55		3901.13			
	Ι	ρ	Ι	$\rho$		
$\lambda = \infty$						
$\nu_1$	111.90	0.04	110.89	0.04		
$\nu_2$	1.10	0.71	1.09	0.73		
$\nu_3$	25.91	0.75	26.13	0.75		
$\lambda = 514.5 \text{ nm}$						
$\nu_1$	124.36	0.04	123.32	0.04		
$\nu_2$	1.05	0.69	1.04	0.71		
$\nu_3$	29.01	0.75	29.3	0.75		
		-				

Table 4. Static and dynamic Raman intensites I ( $\mathring{A}^4$  amu<sup>-1</sup>) and decoherence ratios  $\rho$  for N<sub>2</sub> obtained at various coupled-cluster levels up to FCI using the Sadlej basis. All calculations have been performed at the corresponding equilibrium geometries, bond distances  $r_{\rm NN}$  (in a.u.) and harmonic vibrational frequencies  $\nu_1$  (in cm<sup>-1</sup>) are given as well.

	CCSD	CC3	CCSDT
$r_{ m NN}$	2.10828	2.12139	2.11955
$\nu_1$	2371.30	2293.93	2308.43
$\lambda = \infty$			
Ι	21.19	27.34	24.85
ho	0.07	0.07	0.07
$\lambda = 514.5~\mathrm{nm}$			
Ι	22.87	29.97	27.13
ρ	0.07	0.07	0.07

polarizability with bond distance and in particular of the contributions due to higher excitations are responsible for the effect seen here. Thus, it is not possible to make predictions for the polarizability derivative based on observations for the polarizability, as the geometric perturbation (with orbital relaxation treated ) shows a different behaviour than the electrical perturbations (without treatment of orbital relaxation). We note that previous work by Pecul and co-workers [21] reported the effect of going to CC3 to be about 10%, but their calculations are all performed at the same bondlength, whereas we evaluated the Raman intensities at the equilibrium geometry for each method. Again, no variation in the decoherence ratio is seen.

#### 5 Conclusions

We have presented here, for the first time, a scheme for analytically evaluating Raman intensities for coupled-cluster methods. Furthermore, we have gone beyond any previous work by implementing this for general CC/CI methods, allowing the calculation of Raman intensities at the CCSD, CCSDT, CCSDTQ,...,FCI levels. This work is not only important for the benchmarking of Raman intensities but also represents a step towards full analytic third derivatives in coupled-cluster theory,

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which would allow the evaluation of analytic anharmonic force constants, and the more accurate determination of vibrational spectra. Additionally, the analytic polarizability derivatives made available here can be used to evaluate vibrational contributions to electrical properties (via vibrational averaging of polarizabilities [49] and pure vibrational contributions to hyperpolarizabilities [50]) and provide better estimates for comparison with experimental data.

In the case of Raman intensities, we see that for singly-bonded molecules the inclusion of triple effects is not essential, correcting the CCSD result by only about 1%. In multiple-bonded systems, however, triples are essential for an accurate quantitative description, with the value deviating significantly from the CCSD value. Such effects are to be expected in cases where the increasing multiconfigurational character of the system demands inclusion of higher excitations to compensate for the inadequacy of the reference function. We would expect that quadruple effects are also non-negligible in these cases.

#### 6 Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Hungarian Scientific Research Fund (OTKA) under Contract no. D048583.

#### References

- [1] Pulay, P., 1969, Molec. Phys., 17, 197.
- Pulay, P., 1995, Modern Electronic Structure Theory (World Scientific Publishers), vol. 2, chap. 19. [3] Helgaker, T., 1998, Encyclopedia of computational chemistry (New York: Wiley), chap. Gradient Theory.
- Stanton, J. F. and Gauss, J., 2000, Int. Rev. Phys. Chem., 19, 61.
- [5] Pople, J., Krishnan, R., Schlegel, H., and Binkley, J. S., 1979, Int. J. Quantum Chem., S13, 225.
- [6] Handy, N. C., Amos, R. D., Gaw, J. F., Rice, J. E., Simandiras, E. D., Lee, T. J., Harrison, R. J., Laidig, W. D., Fitzgerald, G. B., and Bartlettt, R. J., 1986, Geometrical Derivatives of Energy Surfaces and Molecular Properties (Dordrecht: Reidel), p. 179.
- [7] Koch, J., Jensen, H. J. A., Jørgensen, P., Helgaker, T., Scuseria, G. E., and Schaefer, H. F., 1990, J. Chem. Phys., 92, 4924.
- Gauss, J. and Stanton, J. F., 1997, Chem. Phys. Lett., 276, 70.
- [9] Kállay, M. and Gauss, J., 2004, J. Chem. Phys., 120, 6841.
- Moccia, R., 1970, Chem. Phys. Lett., 5, 260. [10]
- [11] Pulay, P., 1983, J. Chem. Phys., 78, 5043.
- [12] Gaw, J. F., Yamaguchi, Y., and Schaefer III, H. F., 1984, J. Chem. Phys., 81, 6395.
   [13] Gaw, J. F., Yamaguchi, Y., Schaefer III, H. F., and Handy, N. C., 1986, J. Chem. Phys., 85, 5132.
- 14 Kállay, M. and Gauss, J., 2006, J. Mol. Struct.: THEOCHEM, 768, 71.
- [15] O'Neill, D. P., Kállay, M., and Gauss, J., 2007, Chem. Phys. Lett., submitted.
  [16] Frisch, M. J., Yamaguchi, Y., Gaw, J. F., Schaefer III, H. F., and Binkley, J. S., 1985, J. Chem. Phys., 84. 531.
- Amos, R. D., 1986, Chem. Phys. Lett., 124, 376. [17]
- [18] Van Caillie, C. and Amos, R. D., 2000, Phys. Chem. Chem. Phys., 2, 2123.
- [19] Neugebauer, J., Reiher, M., and Hess, B. A., 2002, J. Chem. Phys., 117, 8623.
- [20] Pecul, M. and Coriani, S., 2002, Chem. Phys. Lett., 355, 327.
- [21] Pecul, M. and Rizzo, A., 2002, J. Chem. Phys., 116, 1259.
- Vidal, L. N. and Vazquez, P. A. M., 2005, Int. J. Quantum. Chem., 103, 632.
- [23] Purvis, G. D. and Bartlett, R. J., 1982, J. Chem. Phys., 76, 1910.
- [24] Koch, H., Christiansen, O., Jørgensen, P., Sanchez de Merás, A. M., and Helgaker, T., 1997, J. Chem. Phys., 106, 1808.
- [25] Kobayashi, R., Koch, H., and Jørgensen, P., 1994, Chem. Phys. Lett., 219, 30.
- Christiansen, O., Gauss, J., and Stanton, J. F., 1998, Chem. Phys. Lett., 292, 437.
- [27] ACESII (Mainz-Austin-Budapest Version), a quantum-chemical program package for high-level calculations of energies and properties by J. F. Stanton et al., see http://www.aces2.de.
- [28] Kállay, M. and Surjan, P. R., 2001, J. Chem. Phys., 115, 2945.
  [29] Kállay, M. and Surjan, P. R., 2000, J. Chem. Phys., 113, 1359.
- MRCC, a generalized CC/CI program by M. Kállay, see http://www.mrcc.hu. [30]
- 31] Placzek, G., 1934, Handbuch der Radiologie (Leipzig: Akademische Verlagsgesellschaft), vol. 6, p. 205.
- Jørgensen, P. and Helgaker, T., 1988, J. Chem. Phys., 89, 1560. Szalay, P. G., 1995, Int. J. Quantum Chem., 55, 151. [32]
- [33]
- [34] Handy, N. C. and Schaefer III, H., 1984, J. Chem. Phys., 81, 5031.

#### Molecular Physics

#### Molecular Physics

- [35] Christiansen, O., Jørgensen, P., and Hättig, C., 1997, Int. J. Quantum Chem., 68, 1.
- [36] Christiansen, O., Hättig, C., and Gauss, J., 1998, J. Chem. Phys., 109, 4745.
- [37] Salter, E. A., Sekino, H., and Bartlett, R. J., 1987, J. Chem. Phys, 87, 502.
  [38] Salter, E. A., Trucks, G. W., and Bartlett, R. J., 1989, J. Chem. Phys., 90, 1752.
- [39] Gauss, J., Stanton, J. F., and Bartlett, R. J., 1991, J. Chem. Phys., 95, 2623.

Raman revised

- [40] Gauss, J. and Stanton, J. F., 1995, J. Chem. Phys., 103, 3561.
  [41] Gauss, J. and Stanton, J. F., 1996, J. Chem. Phys., 104, 2574.
  [42] Stanton, J. F. and Gauss, J., 1997, Recent Advances in Coupled-Cluster Methods (Singapore: World) in Gram Brein Bre Scientific), chap. Analytic Second Derivatives in Coupled-Cluster Theory, p. 49.
- Kállay, M., Gauss, J., and Szalay, P. G., 2003, J. Chem. Phys., 119, 2991. Sadlej, A. J., 1988, Collect. Czech. Chem. Commun., 53, 1995. [43]
- [44][45]
- Sadlej, A. J., 1992, Theor. Chim. Acta, 79, 123. Dunning, T. H., 1989, J. Chem. Phys., 90, 1007. [46]
- Woon, D. E. and Dunning, T. H., 1995, J. Chem. Phys., 100, 2975. [47]
- [48] Halls, M. D. and Schlegel, H. B., 1999, J. Chem. Phys., 111, 8819.
  [49] Buckingham, A. D., 1962, J. Chem. Phys., 36, 3096.
- [50] Bishop, D. M. and Kirtman, B., 1991, J. Chem. Phys., 95, 2646.