

TDHF Evaluation of the Dipole–Quadrupole Polarizability and Its Geometrical Derivatives

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Abstract: Analytical procedures based on the time-dependent Hartree–Fock (TDHF) scheme are elaborated to evaluate the frequency-dependent electric dipole–electric quadrupole polarizability and its derivatives with respect to atomic Cartesian coordinates. On one hand, the mixed second-order TDHF equations are solved iteratively to obtain the second-order derivatives of the linear combination of atomic orbitals coefficients, once with respect to atomic Cartesian coordinates and once with respect to external dynamic electric fields or electric field gradients. On the other hand, taking advantage of the $2n + 1$ rule, the first-order derivatives of A are expressed with respect to atomic Cartesian coordinates in terms of lower-order derivatives. These procedures have been implemented in the GAMESS quantum chemistry package and have been illustrated in the case of several small molecules as well as adamantane.

1. Introduction

The goal of this paper is to present a set of new analytical methods to compute the first-order geometrical derivatives of the electric dipole–electric quadrupole polarizability, denoted A in the following. The electric dipole–electric quadrupole polarizability and its derivatives with respect to atomic Cartesian coordinates or, more specifically, to vibrational normal mode coordinates, Q , are properties governing the interactions between molecules and electromagnetic fields, including thereof the intermolecular interactions.^{1,2} Thus, A and $(\partial A/\partial Q)$ enter in the description of several optical phenomena as well as spectroscopic signatures.

A is related to both the molecular electric dipole, μ , and electric quadrupole, θ , moments, multipole moments which describe a system in weak interactions with external electric fields or with other molecules. The Hamiltonian, which accounts for these interactions, reads¹

$$\mathcal{H} = \mathcal{H}^0 - \mu_{\xi} E_{\xi} - \frac{1}{3} \theta_{\xi\eta} E_{\xi} E_{\eta} - \dots \quad (1)$$

where E_{ξ} and $E_{\xi\eta}$ are components of the electric field and

electric field gradient, respectively, and summations over the repeated indices is implicit. This equation assumes that the quadrupole moment operator is given in the form of a traceless quantity: $\theta_{\xi\eta} = 3/2[q_i(r_{i\xi}r_{i\eta} - r_i^2/3\delta_{\xi\eta})]$. However, in the methodological part, the ‘standard’, Cartesian form, operator, $\theta_{\xi\eta} = 1/2q_i r_{i\xi} r_{i\eta}$, is adopted, both expressions being related by a simple transformation.

The relations between, on the one hand, the electric dipole and quadrupole moments, and, on the other hand, the components of the electric field and electric field gradient are given by¹

$$\mu_{\xi} = \mu_{\xi}^0 + \alpha_{\xi\xi} E_{\xi} + 1/3 A_{\xi,\xi\eta} E_{\xi\eta} + \dots \quad (2)$$

$$\theta_{\xi\eta} = \theta_{\xi\eta}^0 + A_{\xi,\xi\eta} E_{\xi} + \dots \quad (3)$$

where $\alpha_{\xi\xi}$ and $A_{\xi,\xi\eta}$ are tensor elements of the electric dipole–electric dipole and electric dipole–electric quadrupole polarizabilities, respectively; μ_{ξ}^0 and $\theta_{\xi\eta}^0$ are the electric moments in the absence of external fields.

A as well as α are properties relevant to the description of intermolecular interactions and of dielectric properties.^{1,2} $\partial\alpha/\partial Q$ governs the Raman scattering intensities of fundamental transitions in the harmonic approximation.^{3,4} A and $\partial A/\partial Q$ are involved in collision-induced Rayleigh and Raman

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scatterings, respectively.^{5–11} For instance, Elliasmine et al.⁸ obtained a value of $1 \text{ \AA}^4 (= 12.75 \text{ au})$ for the absolute value of A in CF_4 . Its bond length derivative, $|\partial A/\partial R|$, was later deduced from collision-induced Raman experiment by Bancewicz et al.⁹ and attains 5.3 \AA^3 or 35.8 au . These experimental $|A|$ and $|\partial A/\partial R|$ values have been compared to high-level ab initio calculations performed by Maroulis.^{12,13} Combining a numerical finite field approximation with the Møller–Plesset scheme, the best/recommended A value amounts to 12.4 au ,¹³ while the estimated $\partial A/\partial R$ is 27.7 au ,¹² in good agreement with experiment.

The amplitude of the dipole–quadrupole polarizability can also be addressed from high-resolution infrared absorption spectra and in particular from the analysis of the rotational energy levels of the molecule under study interacting with surrounding molecules. Thus, using CH_4 and CD_4 trapped in solid parahydrogen, a $A(\text{CD}_4)/A(\text{CH}_4)$ ratio of 0.875 was determined by Momose and co-workers.^{14,15}

Together with the electric dipole–magnetic dipole polarizability (G'), A describes the electric field-induced differential scattering effect.^{16,17} It is also involved in the description of the electric-field-gradient-induced birefringence.¹⁸ In ref 19, a coupled-perturbed Hartree–Fock (CPHF) scheme is presented to evaluate the static A value. As a preliminary step toward evaluating the derivatives of A wrt Q , the present paper also describes a method for evaluating dynamic A values.

The first-order geometrical derivatives of A enter directly in the determination of the vibrational Raman Optical activity (VROA) intensities together with the first-order geometrical derivatives of α and G' .^{20–26} VROA spectroscopy, which provides molecular structure information on chiral species, is focusing an increasing interest due to its broad range of applications including the determination of absolute configurations²⁷ and the characterization of conformational dynamics in proteins.²⁸ Simulating VROA spectra by means of analytical procedures taking into account the frequency of the incident light brings indeed the main motivation for this work because, so far, the evaluation of the VROA intensities is carried out by using finite difference procedures for part or for all the response properties.

In this work, an analytical procedure is elaborated and implemented for calculating the frequency-dependent $\partial A/\partial Q$ quantities. A similar procedure was previously worked out for the $\partial\alpha/\partial Q$ which are—in addition to the vibrational frequencies—the sole required quantities for simulating Raman spectra in Placzek's approximation. A procedure for evaluating the more cumbersome $\partial G'/\partial Q$ is under development. In addition, within the evaluation of $\partial A/\partial Q$, the Time-dependent Hartree–Fock (TDHF) procedure is applied here, for the first time, to the evaluation of a response property with respect to three different perturbations: the electric fields, electric field gradients, and geometrical distortions. Section 2 presents the methodology and discusses the iterative and less (or partially) iterative schemes. The implementation and the illustration of the methods are described in section 3 before conclusions are drawn in section 4.

2. Methodology

Considering eqs 2 and 3, the elements of the dipole–quadrupole polarizability tensor can be defined either with respect to the quadrupole moment or to the dipole moment

$$A_{\xi,\xi\eta}(-\omega;\omega) = \frac{\partial\theta_{\xi\eta}}{\partial E_{\xi}(-\omega)} \quad (4a)$$

$$= \frac{\partial\mu_{\xi}}{\partial\nabla_{\eta}E_{\xi}(\omega)} \quad (4b)$$

In the first equation, the quadrupole moment, i.e. $\theta_{\xi\eta} = -\text{Tr}[D^0H^{\xi\eta}]$, is differentiated with respect to the dynamic electric field, whereas in the second, the dipole moment, i.e. $\mu_{\xi} = -[\text{Tr}D^0H^{\xi}]$, is differentiated with respect to the dynamic electric field gradient. However, both expressions lead to the same results. Subsequently, the matrix analogues of eqs 4a and 4b read

$$A_{\xi,\xi\eta}(-\omega;\omega) = -\text{Tr}[D^{\xi}(-\omega)H^{\xi\eta}] \quad (5a)$$

$$= -\text{Tr}[H^{\xi}D^{\xi\eta}(\omega)] \quad (5b)$$

H^{ξ} and $H^{\xi\eta}$ are the matrices of the ξ and $\xi\eta$ components of the dipole and quadrupole moments in the atomic orbitals (AO) basis representation, respectively. $D^{\xi}(-\omega)$ and $D^{\xi\eta}(\omega)$ are the first-order derivatives of the density matrix with respect to the electric field component directed along the ξ axis and to the electric field gradient component along the ξ and η axis, both oscillating at frequencies $-\omega$ and ω , respectively. They can be evaluated following the TDHF scheme described by Sekino and Bartlett²⁹ and by Karna and Dupuis^{30,31} to determine electric field derivatives or its generalization to electric field gradient perturbation.

Subsequently, the derivatives of these two expressions with respect to the a Cartesian coordinate are given by

$$\begin{aligned} A_{\xi,\xi\eta}^a(-\omega;\omega) &= \frac{\partial}{\partial a}[A_{\xi,\xi\eta}(-\omega;\omega)] \\ &= -\text{Tr}[D^{\xi,a}(-\omega)H^{\xi\eta} + D^{\xi}(-\omega)H^{\xi\eta,a}] \end{aligned} \quad (6a)$$

$$= -\text{Tr}[H^{\xi,a}D^{\xi\eta}(\omega) + H^{\xi}D^{\xi\eta,a}(\omega)] \quad (6b)$$

$H^{\xi,a}$ and $H^{\xi\eta,a}$ are the a derivatives of the H^{ξ} and $H^{\xi\eta}$ matrices, respectively. $H^{\xi,a}$ is also required to determine the IR intensities. $D^{\xi,a}(-\omega)$ and $D^{\xi\eta,a}(\omega)$ are mixed second-order derivatives of the density matrix. The first can be obtained via the iterative procedure described in ref 32, which provides the frequency-dependent Raman intensities, whereas the procedure to evaluate the second quantities is presented below.

2.1. Basics of the Mixed TDHF Approach. The strategy of refs 32–35 is followed. It combines procedures for evaluating derivatives with respect to oscillating electric fields^{29–31} and with respect to atomic Cartesian coordinates.^{36,37} Therefore, it extends to dynamic perturbations the successive derivative schemes developed in the book of Schaefer and collaborators.³⁸ Several theoretical and methodological aspects related to these mixed dynamic derivatives have recently been reviewed by one of us.³⁹ The starting

point consists of the TDHF equation

$$FC - i \frac{\partial SC}{\partial t} = SC\epsilon \quad (7)$$

the normalization condition of the wave function

$$C^\dagger SC = 1 \quad (8)$$

and the definition of the density matrix

$$D = CnC^\dagger \quad (9)$$

where F , ϵ , S , and C are the Fock matrix, the energy matrix, the overlap matrix, and the linear combination of atomic orbitals (LCAO) matrix, respectively. n is the diagonal matrix of occupation numbers (here, for a closed-shell system, $n_{ii} = 2$ for occupied molecular orbitals and zero otherwise). In addition to the geometrical distortions associated with each of the $3N$ atomic Cartesian coordinates (a)

$$\lambda^a = x_a \quad (10)$$

and the application of an external oscillating electric field oriented along the ξ axis

$$\lambda^\xi = E_\xi e^{i\omega_\xi t} = (\lambda^{-\xi})^* \quad (11)$$

gradient along the η axis of an electric field oriented along the ζ axis is also considered

$$\lambda^{\zeta\eta} = \nabla_\eta E_\xi e^{i\omega_\xi t} = (\lambda^{-\zeta\eta})^* \quad (12)$$

Each matrix is developed with respect to the three kinds of perturbation. For example, the Fock matrix

$$F = F^0 + \sum_i^{\xi, \zeta\eta, a} \lambda^i F^i + \frac{1}{2} \sum_{ij}^{\xi, \zeta\eta, a} \lambda^i \lambda^j F^{ij} + \dots \quad (13)$$

where the summations run not only over all $3N$ coordinates, over all the field directions (x , y , z), and over all the electric field gradient directions (xx , xy , ..., zz) but also over all opposite directions ($-x$, $-y$, $-z$ and $-xx$, $-xy$, ..., $-zz$) in order to obtain, after combination, real electric field and electric field gradient components. For first order in the electric field gradient as well as for mixed second order in the electric field gradient and geometrical distortion, the two sets of equations are

$\lambda^{\zeta\eta}$:

$$F^0 C^{\zeta\eta} + F^{\zeta\eta} C^0 + \omega_{\zeta\eta} S^0 C^{\zeta\eta} = S^0 C^0 \epsilon^{\zeta\eta} + S^0 C^{\zeta\eta} \epsilon^0 \quad (14)$$

$$C^{(-\zeta\eta)\dagger} S^0 C^0 + C^{0\dagger} S^0 C^{\zeta\eta} = 0 \quad (15)$$

$$D^{\zeta\eta} = C^{\zeta\eta} n C^{0\dagger} + C^0 n C^{(-\zeta\eta)\dagger} \quad (16)$$

$\lambda^{\zeta\eta} \lambda^a$:

$$F^0 C^{\zeta\eta, a} + F^{\zeta\eta} C^a + F^a C^{\zeta\eta} + F^{\zeta\eta, a} C^0 + \omega_{\zeta\eta} S^0 C^{\zeta\eta, a} + \omega_{\zeta\eta} S^a C^{\zeta\eta} = S^0 C^0 \epsilon^{\zeta\eta, a} + S^0 C^a \epsilon^{\zeta\eta} + S^a C^0 \epsilon^{\zeta\eta} + S^a C^{\zeta\eta} \epsilon^0 + S^0 C^{\zeta\eta, a} \epsilon^0 + S^0 C^{\zeta\eta} \epsilon^a \quad (17)$$

$$C^{(-\zeta\eta), a\dagger} S^0 C^0 + C^{(-\zeta\eta)\dagger} S^a C^0 + C^{(-\zeta\eta)\dagger} S^0 C^a + C^{a\dagger} S^0 C^{\zeta\eta} + C^{0\dagger} S^a C^{\zeta\eta} + C^{0\dagger} S^0 C^{\zeta\eta, a} = 0 \quad (18)$$

$$D^{\zeta\eta, a} = C^{\zeta\eta, a} n C^{0\dagger} + C^{\zeta\eta} n C^{a\dagger} + C^a n C^{(-\zeta\eta)\dagger} + C^0 n C^{(-\zeta\eta), a\dagger} \quad (19)$$

2.2. Solution of the TDHF Equations. Following the usual strategy, the (mixed) derivatives of the LCAO matrix, $C^{\zeta\eta}$ and $C^{\zeta\eta, a}$, which enter into the definition of the $D^{\zeta\eta}$ and $D^{\zeta\eta, a}$ matrices, are written as products of the unperturbed LCAO matrix and a matrix denoted $U^{\zeta\eta}$ and $U^{\zeta\eta, a}$, respectively,

$$C_n^x(\pm\omega) = \sum_j^{\text{MO}} C_{nj}^0 U_{ji}^x(\pm\omega) \quad (20)$$

where the x subscript stands for any of these derivatives. The derivatives of the Fock matrix are expressed in the MO basis representation, e.g.

$$G_{ij}^x(\pm\omega) = \sum_{rs}^{AO} C_{ir}^{0\dagger} F_{rs}^x(\pm\omega) C_{sj}^0 \quad (21)$$

Then, using the definitions of the U matrices (eq 20), the derivatives of the normalization condition (eqs 15 and 18) are rewritten as follows

$$U^{x\dagger}(\mp\omega) + U^x(\pm\omega) = X^x(\pm\omega) \quad (22)$$

where $X^x(\pm\omega)$ gathers the suborder terms, if any. The latter are defined in the Appendix.

Using eq 22 and following ref 32, it can be shown that only the individual occupied-virtual and virtual-occupied elements of the $U^x(\pm\omega)$ matrices are required to evaluate the derivative of the density matrix. These off-diagonal block elements are obtained by solving the corresponding TDHF eqs 14 and 17. This is done by left multiplying these two equations by $C^{0\dagger}$ and by considering the noncanonical approximation, in which the (mixed) derivatives of the energy matrix is considered block diagonal, i.e., $\epsilon_{ij}^x(\pm\omega) = 0$ with $(i, j) = (j, i) = (\text{occ}, \text{virt})$. Using eqs 20 and 21 as well as related relations, the off-diagonal block elements of the $U^x(\pm\omega)$ are given by

$$U_{ij}^x(\pm\omega) = \frac{G_{ij}^x(\pm\omega) + Q_{ij}^x(\pm\omega)}{\epsilon_j^0 - \epsilon_i^0 \mp \omega} \quad (23)$$

with $Q_{ij}^x(\pm\omega)$ gathering all the suborder terms from eqs 14 and 17. They are defined in the Appendix. $G_{ij}^x(\pm\omega)$ depends on the $U_{ij}^x(\pm\omega)$ matrix elements via eqs 20 and 21 as well as the definition of $F_{rs}^x(\pm\omega)$. Equation 23 is thus solved iteratively by using $1/2 X_{ij}^x(\pm\omega)$ for initializing $U_{ij}^x(\pm\omega)$.

2.3. First-Order Iterative Procedure To Compute $A_{\xi, \zeta\eta}^a(\mp\omega; \pm\omega)$. In this section, the $2n + 1$ rule^{40,41} is used to evaluate the $\text{Tr}[D^{\xi, a}(-\omega)H^{\zeta\eta}]$ term, avoiding the explicit determination of the mixed derivatives of the density matrix. The procedure leading to the less iterative expression is decomposed into the following steps:

1. Left multiply the equivalent eq 19 of ref 32 for the ξ electric field component by $C^{\zeta\eta\dagger}(-\omega)$.

2. Right multiply the adjoint of eq 14 for the $-(\xi\eta)$ component by $C_{ir}^{\xi,a}(-\omega)$.

3. Subtract the result of step 2 from the result of step 1 and take the sum over all diagonal occupied elements.

4. Take the adjoint of the equations resulting from steps 1 and 2, follow step 3, and replace $\pm\omega$ by $\mp\omega$.

5. Sum the equations resulting from steps 3 and 4. The terms multiplying the $F_{rs}^{\xi\eta}(\omega)$ matrix, i.e. $C_{si}^0 C_{ir}^{\xi,a}(\omega) + C_{si}^{\xi,a}(-\omega) C_{ir}^{0\dagger}$, can be rewritten as, $1/2 D_{sr}^{\xi,a}(-\omega) - 1/2 \mathcal{D}_{sr}^{\xi,a}(-\omega)$ with $D_{sr}^{\xi,a}$ and $\mathcal{D}_{sr}^{\xi,a}$ defined in the Appendix.

6. By developing the derivatives of the Fock matrix ($F_{rs}^{\xi\eta}(\omega)$ and $F_{rs}^{\xi,a}(-\omega)$) and by taking advantage of the superproduct between density matrices and two-electron integrals ($D_{sr}^{\xi,a}(-\omega) D_{qp}^{\xi\eta}(\omega) [2J - K]_{pq,rs}^0 = D_{sr}^{\xi\eta}(\omega) - D_{qp}^{\xi,a}(-\omega) [2J - K]_{pq,rs}^0$), one finally obtains

$$A_{\xi,\xi\eta}^a(-\omega;\omega) = - \sum_{r,s}^{\text{AO}} D_{sr}^{\xi}(-\omega) H_{rs}^{\xi\eta,a} + D_{sr}^{\xi\eta}(\omega) H_{rs}^{\xi,a} - \sum_{p,q,r,s}^{\text{AO}} D_{sr}^{\xi\eta}(\omega) D_{qp}^{\xi}(-\omega) [2J - K]_{pq,rs}^a - 2 \sum_{i,j}^{\text{MO}} \mathcal{U}_{ij}^{\xi,a}(-\omega) G_{ji}^{\xi\eta}(\omega) + \mathcal{U}_{ij}^{\xi\eta,a}(\omega) G_{ji}^{\xi}(-\omega) + \mathcal{U}_{ij}^{\xi,\xi\eta}(-\omega,\omega) G_{ji}^a - 2 \sum_i^{\text{occ}} \omega \mathcal{J}_i^{\xi,\xi\eta,a}(-\omega,\omega) + \mathcal{X}_i^{\xi,\xi\eta,a}(-\omega,\omega) \epsilon_i^0 - 2 \sum_{i,j}^{\text{occ}} X_{ij}^{\xi,a}(-\omega) \epsilon_{ji}^{\xi\eta}(\omega) + X_{ij}^{\xi\eta,a}(\omega) \epsilon_{ji}^{\xi}(-\omega) + X_{ij}^{\xi,\xi\eta}(-\omega,\omega) \epsilon_{ji}^a \quad (24)$$

Intermediate quantities are defined in the Appendix. The last expression requires only first-order derivatives of the wave function with respect to the atomic Cartesian coordinates, the electric field components, or their gradients.

The procedure to evaluate the $\text{Tr}[H^{\xi} D^{\xi\eta,a}(\omega)]$ term, avoiding the explicit determination of $D^{\xi\eta,a}(\omega)$, leads to the same expression of $A_{\xi,\xi\eta}^a(-\omega;\omega)$ (eq 24). This is achieved by adopting the same procedure as described above, besides the interchange of the field and field gradient indices and of their associated pulsations. In other words, this means that eq 24 is symmetric with respect to the field indices and the field gradient indices.

3. Implementation and Results

All these procedures have been implemented into the GAMESS quantum chemistry package⁴² within the TDHFX module and have been checked against a numerical finite distortion scheme. In the later, the dipole–quadrupole polarizability is evaluated for distorted structures along the different vibrational normal coordinates, and the derivatives are evaluated using finite difference expressions. The amplitude of the Cartesian displacements amounts to ± 0.01 ,

Table 1. Relative CPU Time for Evaluating the $\partial A/\partial Q$ Quantities Using the Analytical Iterative and Numerical Differentiation Schemes^a

molecule	analytical/ iterative	method	
		one mode	all modes
methane	3	$0.23 \times 8 = 1.8$	$0.23 \times 8 \times 9 = 17$
adamantane	48	$0.16 \times 8 = 1.3$	$0.16 \times 8 \times 72 = 92$

^a The CPU ratios are given with respect to the CPU times for the less-iterative ($2n + 1$) procedure. The calculations were performed on V60x of SUN Microsystems. The less-iterative procedure took 5.4 and 261.4 min for methane and adamantane, respectively.

± 0.02 , ± 0.04 , and ± 0.08 au, while the Romberg quadrature⁴³ is employed in order to increase the accuracy on the numerical derivatives. Within the given precision of 10^{-5} au both the numerical and analytical derivative schemes provide the same values. In addition, the iterative and the less iterative procedures give the same results within the numerical threshold (10^{-7}). The CPU time ratios between the two types of analytical procedures are greater than one in favor of the less iterative one (Table 1). It increases with the size of the system. As expected, the numerical procedure is, computation-wise, the less advantageous one, except when considering a reduced set of modes of interest.

For illustration purpose, these methods are applied to the determination of the A and $(\partial A/\partial Q)_0$ quantities of three reference systems of T_d symmetry, methane (CH_4), tetrafluoromethane (CF_4), and adamantane ($\text{C}_{10}\text{H}_{16}$) as well as for three other molecules of other symmetry: water (H_2O , C_{2v}), ammonia, (NH_3 , C_{3v}), and benzene (C_6H_6 , D_{6h}). For the molecules of T_d symmetry, the electric dipole–electric quadrupole polarizability tensor possesses only one independent component, $A_{x,y,z}$, provided the standard orientation is adopted. Moreover, the derivatives of $A_{x,y,z}$ with respect to the vibrational normal coordinates present a nonzero value, independent of the permutation of the x , y , and z indices, only for the totally symmetric modes. These two quantities, $A_{x,y,z}$ and $\partial A_{x,y,z}/\partial Q$, are determined within collision-induced light scattering and high-resolution infrared absorption spectroscopies.^{8,9,14,15} However, for modes of T_2 symmetry, the independent/invariant quantity is the norm of the vector part of the $\partial A/\partial Q$ tensor. Following the expression of Zyss⁴⁴ for tensors of rank 3, it reads

$$X_{\text{vec}} = \sqrt{X_x^2 + X_y^2 + X_z^2} \quad (25)$$

with

$$X_i = \frac{1}{3} \sum_j^{x,y,z} X_{i,jj} + X_{j,ij} + X_{jji} \quad (26)$$

where X stands for A or $\partial A/\partial Q$. These results are listed in Tables 2–3, 4–5, and 6–7 for methane, tetrafluoromethane, and adamantane, respectively.

The calculations on CH_4 and CF_4 are carried out using the cc-pvdz and aug-cc-pvdz basis sets.⁴⁵ For adamantane, the DV0 basis set used in ref 46 has been chosen. For comparison purposes, the electric dipole–electric dipole polarizability and its vibrational normal coordinate deriva-

Table 2. Frequency Dispersion of the Dipole–Dipole and Dipole–Quadrupole Polarizabilities and Their Derivatives with Respect to Normal Coordinates of A_1 Symmetry for the Methane Molecule (cc-pvdz and aug-cc-pvdz Basis Sets)^a

ω	cc-pvdz		aug-cc-pvdz	
	$\bar{\alpha}$	$\frac{\partial \bar{\alpha}}{\partial Q}$ $\bar{\nu} = 3165$	$\bar{\alpha}$	$\frac{\partial \bar{\alpha}}{\partial Q}$ $\bar{\nu} = 3152$
0.00	13.012774	−0.159903	15.998164	0.185984
0.02	13.028341	−0.160293	16.018242	0.186443
0.04	13.075335	−0.161472	16.078860	0.187832
0.06	13.154650	−0.163473	16.181196	0.190192
0.08	13.267828	−0.166352	16.327290	0.193592
0.10	13.417141	−0.170190	16.520168	0.198139
$A_{\alpha}, A_{\partial A/\partial Q}$	2.98	6.07	3.13	6.14

ω	$A_{x,yz}$	$\frac{\partial A_{x,yz}}{\partial Q}$ $\bar{\nu} = 3165$	$A_{x,yz}$	$\frac{\partial A_{x,yz}}{\partial Q}$ $\bar{\nu} = 3152$
0.00	14.405079	−0.327439	9.476620	0.246624
0.02	14.431805	−0.328285	9.498117	0.247390
0.04	14.512530	−0.330848	9.563175	0.249713
0.06	14.648930	−0.335194	9.673527	0.253670
0.08	14.843897	−0.341444	9.832198	0.259398
0.10	15.101692	−0.349775	10.043725	0.267104
$A_A, A_{\partial A/\partial Q}$	4.63	6.44	5.65	7.73

^a All the values are given in atomic units (1 au of $\alpha = 1.6488 \times 10^{-41}$ C² m² J^{−1} and 1 au of $A = 8.724958 \times 10^{-52}$ C² m³ J^{−1}), besides the vibrational pulsation in cm^{−1}.

Table 3. Frequency Dispersion of the Derivatives of the Dipole–Quadrupole Polarizabilities with Respect to Normal Coordinates of T_2 Symmetry for the Methane Molecule (cc-pvdz and aug-cc-pvdz Basis Sets)^a

ω	cc-pvdz ($\partial A/\partial Q$) _{vec}		aug-cc-pvdz ($\partial A/\partial Q$) _{vec}	
	$\bar{\nu} = 1434$	$\bar{\nu} = 3285$	$\bar{\nu} = 1425$	$\bar{\nu} = 3265$
0.00	0.215050	0.599220	0.247610	0.787832
0.02	0.215558	0.600470	0.248196	0.789531
0.04	0.217097	0.604252	0.249971	0.794670
0.06	0.219709	0.610662	0.252993	0.803389
0.08	0.223471	0.619866	0.257362	0.815931
0.10	0.228497	0.632115	0.263231	0.832658
$A_{\partial A/\partial Q}$	5.88	5.20	5.88	5.37

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{−1}.

tives are also evaluated following the procedure described in ref 32. Only the average value—corresponding to one-third of the trace of the polarizability tensor—and its derivatives with respect to totally symmetric modes are considered.

For the water and ammonia molecules, the computations have been carried out with the aug-cc-pvdz basis set, whereas for the benzene, the DV0 basis set has been used. Only the nonzero vector components, or the mean value for degenerate modes, are reported. In water, the nonzero quantities are A_z , ($\partial A/\partial Q$)_z for the A_1 bending and symmetric stretching modes, and ($\partial A/\partial Q$)_y for the B_2 asymmetric stretching mode. In the case of ammonia, A_z is different from zero as well as ($\partial A/\partial Q$)_z for the A_1 modes and ($\partial A/\partial Q$)_x = ($\partial A/\partial Q)_y, denoted hereafter ($\partial A/\partial Q$)_(x=y), for the degenerate E modes. Finally,$

Table 4. Frequency Dispersion of the Dipole–Dipole and Dipole–Quadrupole Polarizabilities and Their Derivatives with Respect to Normal Coordinates of A_1 Symmetry for the Tetrafluoromethane Molecule (cc-pvdz and aug-cc-pvdz Basis Sets)^a

ω	cc-pvdz		aug-cc-pvdz	
	$\bar{\alpha}$	$\frac{\partial \bar{\alpha}}{\partial Q}$ $\bar{\nu} = 996$	$\bar{\alpha}$	$\frac{\partial \bar{\alpha}}{\partial Q}$ $\bar{\nu} = 982$
0.00	10.989920	−0.023478	16.162236	0.031226
0.02	10.994104	−0.023507	16.169889	0.031263
0.04	11.006682	−0.023592	16.192911	0.031373
0.06	11.027736	−0.023735	16.231501	0.031559
0.08	11.057400	−0.023938	16.285995	0.031821
0.10	11.095869	−0.024202	16.356875	0.032165
$A_{\alpha}, A_{\partial A/\partial Q}$	0.95	3.02	1.18	2.93

ω	$A_{x,yz}$	$\frac{\partial A_{x,yz}}{\partial Q}$ $\bar{\nu} = 996$	$A_{x,yz}$	$\frac{\partial A_{x,yz}}{\partial Q}$ $\bar{\nu} = 982$
0.00	12.838830	−0.077774	10.943045	0.073150
0.02	12.845476	−0.077855	10.950699	0.073243
0.04	12.865457	−0.078096	10.973717	0.073522
0.06	12.898904	−0.078502	11.012271	0.073991
0.08	12.946040	−0.079075	11.066651	0.074656
0.10	13.007180	−0.079822	11.137268	0.075525
$A_A, A_{\partial A/\partial Q}$	1.29	2.58	1.75	3.16

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{−1}.

Table 5. Frequency Dispersion of the Derivatives of the Dipole–Quadrupole Polarizabilities with Respect to Normal Coordinates of T_2 Symmetry for the Tetrafluoromethane Molecule (aug-cc-pvdz Basis Sets)^a

ω	cc-pvdz ($\partial A/\partial Q$) _{vec}		aug-cc-pvdz ($\partial A/\partial Q$) _{vec}	
	$\bar{\nu} = 686$	$\bar{\nu} = 1448$	$\bar{\nu} = 671$	$\bar{\nu} = 1414$
0.00	0.034040	0.076902	0.044925	0.183403
0.02	0.034073	0.077016	0.044974	0.183637
0.04	0.034171	0.077358	0.045122	0.184342
0.06	0.034337	0.077933	0.045371	0.185528
0.08	0.034571	0.078747	0.045724	0.187211
0.10	0.034876	0.079809	0.046185	0.189416
$A_{\partial A/\partial Q}$	2.40	3.69	2.73	3.18

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{−1}.

A of benzene is zero. The nonzero ($\partial A/\partial Q$) terms are associated with the E_{1u} and A_{2u} modes. These results are given in Tables 8–10 for water, ammonia, and benzene, respectively.

The effects of the frequency have been addressed by performing calculations with a pulsation of the external electric field (or electric field gradient) ranging between 0.00 and 0.10 au. This corresponds to a photon energy ranging between 0.0 and 2.71 eV or a wavelength between ∞ and 456 nm. The frequency effects are characterized by the coefficients (A , B , ...) of the power series expansion in ω^2 :

$$\alpha(-\omega;\omega) = \alpha(0;0)[1 + A_{\alpha}\omega^2 + B_{\alpha}\omega^4 + \dots] \quad (27)$$

$$A(-\omega;\omega) = A(0;0)[1 + A_A\omega^2 + B_A\omega^4 + \dots] \quad (28)$$

Table 6. Frequency Dispersion of the Dipole–Dipole and Dipole–Quadrupole Polarizabilities and Their Derivatives with Respect to Normal Coordinates of A_1 Symmetry for the Adamantane Molecule (DV0 Basis Set)^a

ω	$\bar{\alpha}$	$\partial\bar{\alpha}/\partial Q$				
		$\bar{\nu} = 805$	$\bar{\nu} = 1149$	$\bar{\nu} = 1679$	$\bar{\nu} = 3057$	$\bar{\nu} = 3114$
0.00	89.821106	0.092692	0.002022	0.009827	0.045178	0.354509
0.02	89.909246	0.092874	0.002019	0.009846	0.045243	0.355170
0.04	90.174820	0.093423	0.002011	0.009904	0.045438	0.357163
0.06	90.621335	0.094352	0.001998	0.010002	0.045769	0.360529
0.08	91.254776	0.095676	0.001977	0.010140	0.046241	0.365331
0.10	92.083824	0.097425	0.001950	0.010320	0.046866	0.371668
$A_\alpha, A_{\partial\alpha/\partial Q}$	2.45	4.90	−3.26	4.90	3.57	4.65

ω	$A_{x,yz}$	$\partial A_{x,yz}/\partial Q$				
		$\bar{\nu} = 805$	$\bar{\nu} = 1149$	$\bar{\nu} = 1679$	$\bar{\nu} = 3057$	$\bar{\nu} = 3114$
0.00	9.736843	−0.074647	−0.080733	0.026879	1.774280	0.035720
0.02	9.741735	−0.074856	−0.080809	0.027157	1.778279	0.035569
0.04	9.756504	−0.075487	−0.081038	0.027999	1.790362	0.035112
0.06	9.781434	−0.076557	−0.081424	0.029425	1.810798	0.034332
0.08	9.817037	−0.078091	−0.081974	0.031475	1.840048	0.033203
0.10	9.864102	−0.080128	−0.082696	0.034204	1.878795	0.031684
$A_A, A_{\partial A/\partial Q}$	1.25	6.97	2.35	25.78	5.62	−10.51

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{-1} .**Table 7.** Frequency Dispersion of the Derivatives of the Dipole–Quadrupole Polarizabilities with Respect to Normal Coordinates of T_2 Symmetry for the Adamantane Molecule (DV0 Basis Set)^a

ω	$(\partial A/\partial Q)_{\text{vec}}$				
	$\bar{\nu} = 508$	$\bar{\nu} = 722$	$\bar{\nu} = 866$	$\bar{\nu} = 1083$	$\bar{\nu} = 1248$
0.00	0.000084	0.076755	0.418069	0.166360	0.046304
0.02	0.000039	0.076967	0.418903	0.166730	0.046355
0.04	0.000095	0.077607	0.421422	0.167849	0.046509
0.06	0.000319	0.078689	0.425680	0.169741	0.046768
0.08	0.000634	0.080238	0.431766	0.172452	0.047132
0.10	0.001044	0.082287	0.439814	0.176048	0.047605
$A_{\partial A/\partial Q}$	/	6.88	4.97	5.44	2.77

ω	$(\partial A/\partial Q)_{\text{vec}}$					
	$\bar{\nu} = 1505$	$\bar{\nu} = 1555$	$\bar{\nu} = 1659$	$\bar{\nu} = 3062$	$\bar{\nu} = 3089$	$\bar{\nu} = 3123$
0.00	0.203037	0.628231	0.358723	0.557977	3.347433	1.345444
0.02	0.203447	0.629240	0.359324	0.558745	3.353880	1.347922
0.04	0.204684	0.632285	0.361137	0.561059	3.373355	1.355409
0.06	0.206770	0.637421	0.364192	0.564955	3.406265	1.368063
0.08	0.209744	0.644743	0.368541	0.570492	3.453312	1.386158
0.10	0.213660	0.654390	0.374259	0.577756	3.515531	1.410099
$A_{\partial A/\partial Q}$	5.04	4.01	4.18	3.43	4.80	4.59

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{-1} .

which are determined by least-squares fittings. In all cases, the resulting correlation coefficient (R^2) is larger than 0.999. The results are listed in Tables 2 and 3, 4 and 5, and 6 and 7 for CH_4 , CF_4 , and adamantane, respectively, for modes having A_1 (T_2) symmetry. The results for water, ammonia, and benzene are listed in Tables 8–10, respectively. A brief discussion of these results is given below.

Methane. The static (CPHF) aug-cc-pvdz A ($=A_{x,yz}$) value (9.48 au) is in good agreement with the SCF results of Maroulis,^{13,47} who pointed out that electron correlation effects are small and mostly accounted for at the MP2 level: the SCF, MP2, and CCSD(T) values from ref 13 are 9.48, 8.98, and 9.03 au, respectively. A increases with the frequency

faster than $\bar{\alpha}$ as demonstrated by the larger value of A_A with respect to A_α . The frequency dispersion is also stronger for $\partial A/\partial Q$ than for $\partial\alpha/\partial Q$. Although it is not the main focus of the present investigation, the experimental A value determined by Buck et al.⁴⁸ is a bit larger and attains 11.3 au.

Tetrafluoromethane. The static aug-cc-pvdz A value (10.94 au) of CF_4 is slightly larger than for CH_4 , but its frequency dispersion is smaller. At the SCF level, Maroulis obtained a value of 11.15 au, while including electron correlation at the MP2 and MP4 levels¹² (different basis sets are used for evaluating the SDQ and T fourth-order corrections) leads to A values of 12.00 and 12.27 au, respectively. The agreement with the experimentally derived values of

Table 8. Frequency Dispersion of the Nonzero Vector Component of the Dipole–Quadrupole Polarizability and Its Derivatives with Respect to Normal Coordinates for the Water Molecule (aug-cc-pvdz Basis Set)^a

ω	A_z	$(\partial A/\partial Q)_z$ $\bar{\nu} = 1742$ (A_1)	$(\partial A/\partial Q)_z$ $\bar{\nu} = 4133$ (A_1)	$(\partial A/\partial Q)_y$ $\bar{\nu} = 4236$ (B_2)
0.00	-6.158025	0.109973	-0.310840	0.344829
0.02	-6.168362	0.110137	-0.311397	0.345375
0.04	-6.199663	0.110632	-0.313083	0.347027
0.06	-6.252817	0.111469	-0.315945	0.349825
0.08	-6.329399	0.112668	-0.320066	0.353841
0.10	-6.431829	0.114261	-0.325575	0.359187
$A, A_{\partial A/\partial Q}$	4.18	3.71	4.46	3.94

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{-1} .

Table 9. Frequency Dispersion of the Nonzero Vector Component of the Dipole–Quadrupole Polarizability and Its Derivatives with Respect to Normal Coordinates for the Ammonia Molecule (aug-cc-pvdz Basis Set)^a

ω	A_z	$(\partial A/\partial Q)_z$ $\bar{\nu} = 1105$ (A_1)	$(\partial A/\partial Q)_{(x=y)}$ $\bar{\nu} = 1765$ (E)	$(\partial A/\partial Q)_z$ $\bar{\nu} = 3685$ (A_1)	$(\partial A/\partial Q)_{(x=y)}$ $\bar{\nu} = 3815$ (E)
0.00	4.967627	0.148364	0.150261	0.344611	0.495260
0.02	4.978129	0.148619	0.150576	0.345387	0.496125
0.04	5.010083	0.149386	0.151533	0.347739	0.498741
0.06	5.064903	0.150680	0.153164	0.351737	0.503179
0.08	5.145182	0.152521	0.155527	0.357502	0.509565
0.10	5.255131	0.154933	0.158718	0.365222	0.518092
$A, A_{\partial A/\partial Q}$	5.24	4.29	5.22	5.61	4.35

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{-1} .

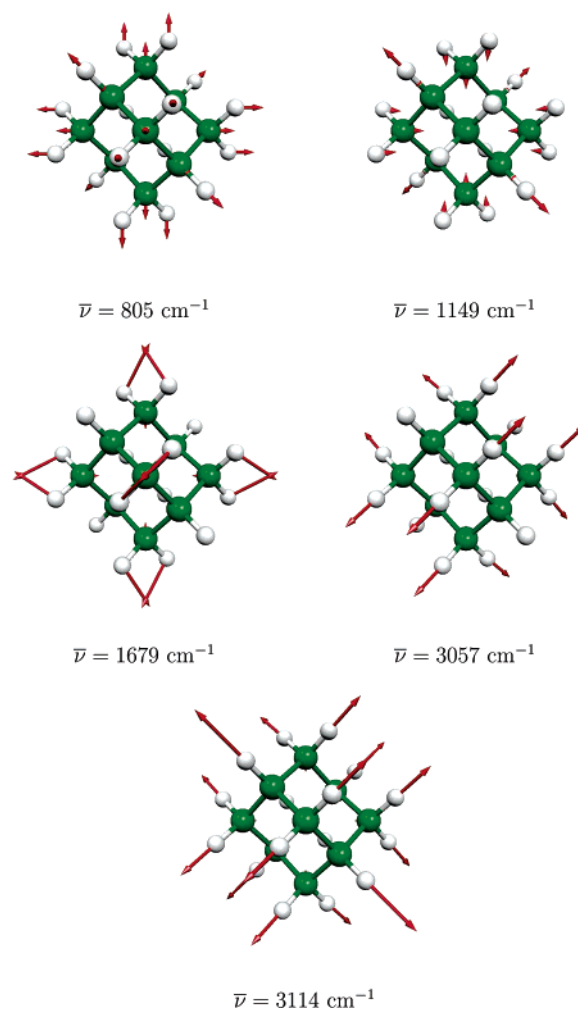
Table 10. Frequency Dispersion of the Nonzero Vector Components of the Derivatives with Respect to Normal Coordinates of the Dipole–Quadrupole Polarizabilities for the Benzene Molecule (DVO Basis Set)^a

ω	$(\partial A/\partial Q)_z$ $\bar{\nu} = 781$ (A_{2u})	$(\partial A/\partial Q)_{(x=y)}$ $\bar{\nu} = 1138$ (E_{1u})	$(\partial A/\partial Q)_{(x=y)}$ $\bar{\nu} = 1636$ (E_{1u})	$(\partial A/\partial Q)_{(x=y)}$ $\bar{\nu} = 3407$ (E_{1u})
0.00	-0.088044	0.346603	0.492332	2.355252
0.02	-0.089535	0.348050	0.494174	2.359332
0.04	-0.094116	0.352482	0.499819	2.371645
0.06	-0.102127	0.360183	0.509648	2.392409
0.08	-0.114196	0.371684	0.524369	2.421996
0.10	-0.131353	0.387857	0.545154	2.460949
$A_{\partial A/\partial Q}$	41.7	10.3	9.21	4.32

^a All the values are given in atomic units, besides the vibrational pulsation in cm^{-1} .

Elliasmine et al.⁸ (12.75 au) is very good. In what concerns $\partial A/\partial Q$ of CF_4 , both its static value and its frequency dispersion are smaller than in the case of methane. On the other hand, similar to methane, the frequency dispersions of A and $\partial A/\partial Q$ are stronger than for α and $\partial \alpha/\partial Q$, respectively. The corresponding $\partial A/\partial R$, which can be deduced from $\partial A/\partial Q$, where Q is the normal coordinate of the totally symmetric vibration, amounts to the same value of 27.7 au as in ref 12 in the static limit.

Basis Set Effects. The inclusion of diffuse and polarized functions, characterizing the passage from the cc-pvdz to aug-cc-pvdz basis sets, produces opposite effects upon the

**Figure 1.** Schematic representations of the totally symmetric vibrational normal modes of adamantane.

dipole–dipole and dipole–quadrupole polarizability responses and their derivatives with respect to totally symmetric modes. On the one hand, an increase of the $\bar{\alpha}$ and $\partial \bar{\alpha}/\partial Q$ quantities is observed, and this effect is much important for tetrafluoromethane (+47% and +33%) than for methane (+22% and +16%). On the other hand, a much important decrease of the $A_{x,yz}$ and $\partial A_{x,yz}/\partial Q$ quantities is ascertained for methane (−34% and −25%) than for tetrafluoromethane (−15% and −6%). Moreover, a general increase of the frequency dispersion coefficients is also observed with the exception of $A_{\bar{\alpha}}$ of CF_4 which decreases by going from cc-pvdz to aug-cc-pvdz. For the modes belonging to the T_2 symmetry, the $(\partial A/\partial Q)_{\text{vec}}$ quantity is more sensitive to the choice of the basis set than the (x, yz) tensor component, and this effect is much important for CF_4 (+32% and +138%) than for CH_4 (+15% and +31%). However, the corresponding frequency dispersion coefficients vary less. Since expressions for geometrical derivatives of the two-electron integrals between atomic orbitals are not implemented in the GAMESS package for f, g, \dots type functions, further systematic investigation of the basis set effects (i.e. considering aug-cc-pvtz, ...) is presently nonfeasible.

Adamantane. The value of the electric dipole–electric quadrupole polarizability of adamantane as calculated at the

TDHF level of approximation is of similar magnitude as for the CH₄ and CF₄ molecules. The electric-dipole–electric-dipole polarizability—which displays a closer relationship to the molecular size or volume—of adamantane is however much larger than for CH₄ and CF₄, as expected from the larger size of the former. Besides the sign, A values of similar magnitude have been evaluated in ref 46, whereas the value determined from collision-induced light scattering experiment is much larger (-102.0 ± 7.8 au). Again, like for CH₄ and CF₄, the variations in the frequency of A are smaller than for α . The situation is different for the $\partial A/\partial Q$ and $\partial \alpha/\partial Q$ quantities. In addition, for the 1149 and 3144 cm⁻¹ modes, the $\partial \alpha/\partial Q$ and $\partial A/\partial Q$ quantities decrease with the frequency, respectively. The different totally symmetric vibrational modes of adamantane are sketched in Figure 1. From Table 6, it also turns out that the larger $\partial A/\partial Q$ value is associated with the 3057 cm⁻¹ mode, while for $\partial \alpha/\partial Q$, it is the 3114 cm⁻¹ mode. With the exception of the 508 cm⁻¹ mode which shows a nonmonotonic behavior with respect to ω , all the other T_2 symmetry modes present frequency dispersion coefficients of similar amplitude to those for $\partial A/\partial Q_{A_1}$.

Water, Ammonia, and Benzene. Numerical illustrations are also provided for the A and $(\partial A/\partial Q)$ quantities of water, ammonia, and benzene. The A_z amplitude of H₂O is larger than for NH₃, but its frequency dispersion is smaller. The $\partial A/\partial Q$ values and their evolution with frequency are similar for both H₂O and NH₃. For benzene, the A frequency dispersion coefficients are particularly large. To our knowledge, no experimental data are available for these three systems.

4. Conclusions

Analytical procedures based on the time-dependent Hartree–Fock (TDHF) scheme are elaborated to evaluate the frequency-dependent electric dipole–electric quadrupole polarizability (A) and its derivatives with respect to atomic Cartesian coordinates and vibrational normal coordinates ($\partial A/\partial Q$). On one hand, the mixed second-order TDHF equations are solved iteratively to obtain the second-order derivatives of the linear combination of atomic orbitals coefficients, once with respect to atomic Cartesian coordinates and once with respect to external dynamic electric fields or electric field gradients. On the other hand, taking advantage of the $2n + 1$ rule, the first-order derivatives of A with respect to atomic Cartesian coordinates are expressed in terms of lower-order derivatives. These procedures are implemented in the GAMESS quantum chemistry package and are illustrated in the case of several small molecules as well as adamantane.

The frequency dispersion of $\partial A/\partial Q$ (and A) is shown to be of the same order of magnitude as for $\partial \alpha/\partial Q$ (and α). Thus, in addition to the importance of taking into account explicitly the pulsation of the incident light in Raman simulations,^{32,49,50} the evaluation of $\partial A/\partial Q$, which enters in the determination of the VROA intensities, should also consider explicitly the pulsation. A comparison between the cc-pvdz and aug-cc-pvdz basis sets further demonstrates that diffuse functions may have opposite effects on the dipole–dipole (α , $\partial \alpha/\partial Q$) and dipole–quadrupole (A , $\partial A/\partial Q$) responses. To our knowledge, this is the first time that the TDHF scheme is applied to the evaluation of a response

property with respect to three different perturbations and thus to the analytical evaluation of $\partial A/\partial Q$.

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Appendix: Definitions of Quantities

In the following expressions, the Einstein convention is assumed throughout, and, unless specified, the sums run over (occupied and unoccupied) molecular orbitals.

$$X_{ij}^{\zeta\eta}(\omega) = 0 \quad (29)$$

$$Q_{ij}^{\zeta\eta}(\omega) = 0 \quad (30)$$

$$X_{ij}^{\zeta\eta,a}(\omega) = U_{ik}^a U_{kj}^{\zeta\eta}(\omega) - U_{ik}^{\zeta\eta}(\omega) U_{kj}^{a\dagger} \quad (31)$$

$$Q_{ij}^{\zeta\eta,a}(\omega) = G_{ik}^{\zeta\eta}(\omega) U_{kj}^a + U_{ik}^{a\dagger} \epsilon_{kj}^{\zeta\eta}(\omega) + G_{ik}^a U_{kj}^{\zeta\eta}(\omega) - U_{ik}^{\zeta\eta}(\omega) \epsilon_{kj}^a + I_{ik}^a U_{kj}^{\zeta\eta}(\omega) [\omega - \epsilon_j^0] \quad (32)$$

where $I_{ij}^a = \sum_{rs} A_{rs}^O C_{ir}^{0\dagger} S_{rs}^a C_{sj}^0$ is the derivative of the overlap matrix in the MO basis representation. The U^a matrix elements are evaluated using the CPHF scheme of refs 36 and 37.

$$J_i^{\xi,\zeta\eta,a}(-\omega, \omega) = U_{ik}^{\zeta\eta\dagger}(-\omega) I_{kl}^a U_{li}^{\xi}(-\omega) - U_{ik}^{\xi\dagger}(\omega) I_{kl}^a U_{li}^{\zeta\eta}(\omega) \quad (33)$$

$$Q_{ij}^{\xi,\zeta\eta,a}(-\omega, \omega) = -U_{ik}^{\zeta\eta\dagger}(-\omega) I_{kl}^a U_{li}^{\xi}(-\omega) - U_{ik}^{\xi\dagger}(\omega) I_{kl}^a U_{li}^{\zeta\eta}(\omega) \quad (34)$$

$$X_{ij}^{\xi,\zeta\eta}(-\omega, \omega) = -U_{ik}^{\zeta\eta\dagger}(-\omega) U_{kj}^{\xi}(-\omega) - U_{ik}^{\xi\dagger}(\omega) U_{kj}^{\zeta\eta}(\omega) \quad (35)$$

$$\mathcal{U}_{ij}^{\zeta\eta,a}(\omega) = \sum_k^{\text{occ}} U_{ik}^a U_{kj}^{\zeta\eta}(-\omega) + U_{ik}^{\zeta\eta}(\omega) U_{kj}^{a\dagger} \quad (36)$$

$$\mathcal{U}_{ij}^{\xi,\zeta\eta}(-\omega, \omega) = \sum_k^{\text{occ}} U_{ik}^{\xi}(-\omega) U_{kj}^{\zeta\eta\dagger}(-\omega) + U_{ik}^{\zeta\eta}(\omega) U_{kj}^{\xi\dagger}(-\omega) \quad (37)$$

$$\mathcal{U}_{ij}^{\xi,a}(-\omega) = \sum_k^{\text{occ}} U_{ik}^a U_{kj}^{\xi\dagger}(-\omega) + U_{ik}^{\xi}(\omega) U_{kj}^{a\dagger} \quad (38)$$

$$X_{ij}^{\xi,a}(-\omega) = U_{ik}^a U_{kj}^{\xi}(\omega) - U_{ik}^{\xi}(\omega) U_{kj}^{a\dagger} \quad (39)$$

$$D^{\xi,a}(\omega) = C^{\xi,a}(\omega) n C^{0\dagger} + C^0 n C^{(-\xi),a\dagger} + \mathcal{D}^{\xi,a}(-\omega) \quad (40)$$

$$\mathcal{D}^{\xi,a}(\omega) = C^{\xi}(\omega) n C^{a\dagger} + C^a n C^{(-\xi)\dagger}(-\omega) \quad (41)$$

The $U^{\zeta}(\omega)$ matrix elements are evaluated using the TDHF approach of refs 29–31.

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