Analytic Calculations of Vibrational Hyperpolarizabilities in the Atomic Orbital Basis

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We present an analytic scheme for the calculation of pure vibrational contributions to linear and nonlinear optical properties such as the polarizability and the first and second hyperpolarizabilities. The formalism is fully expressed in terms of a perturbation- and time-dependent atomic orbital basis, using the elements of the density matrix in the atomic orbital basis as the basic variables. We calculate perturbed densities up to third order with respect to the electric field in accordance with the $n + 1$ rule, and the approach is therefore applicable for the calculation of pure vibrational contributions involving all vibrational coordinates in large molecular complexes. In the case of static electric fields, we therefore only need to calculate 19 response equations, independent of the size of the molecule. If we can determine the molecular energy and force field, the calculation of pure vibrational contributions to the nonlinear optical properties of the molecule is therefore a rather straightforward task. We illustrate the implementation by calculating pure vibrational contributions to the first and second hyperpolarizabilities of molecules containing up to 66 atoms using basis sets of good quality.

I. Introduction

Nonlinear optical properties of organic molecules have received increasing interest in recent years, experimentally as well as theoretically. The possibilities offered by combining the flexible material properties of organic molecules with the applicability of materials with large nonlinear optical properties in fields such as noninvasive imaging, 3-dimensional optical data storage and optical power limiting, have led to a steadily increasing research effort in these fields of science (see, e.g., ref 1 and references therein).

Whereas much attention has been paid to the electronic contributions to the hyperpolarizabilities, arising either from multiphoton virtual excitations in the electronic manifold of the molecules or from multiphoton absorption processes,[2] many theoretical studies have demonstrated that the nonlinear optical processes arising from excitations within the vibrational manifold may be as large as, and in some cases even dominate, the electronic contributions.[3,4] It is generally recognized that these *pure vibrational contributions* are most significant when static electric fields enter the nonlinear optical process, such as electric field-induced second-harmonic generation or electro-optical Pockels or Kerr effects.[5] The pure vibrational effects are thus particularly large in the case of the static hyperpolarizabilities.

Several approaches have been introduced to calculate pure vibrational contributions. The first study that paved the way for a large number of calculations of pure vibrational contributions to hyperpolarizabilities was the perturbation theory approach of Bishop and Kirtman.[6,7] In this approach, the potential energy surface and the properties are expanded in a Taylor series around the molecular equilibrium geometry along the different normal coordinates of the molecule. As a consequence, the approach requires the calculation of geometrical derivatives of the molecular energy as well as the dipole moment and the (hyper)polarizabilities. Until recently, the lack of analytical methods for calculating these polarizability derivatives prevented studies on larger molecules. The development of an analytical scheme for calculating first-order geometrical derivatives of the polarizability[8] and first hyperpolarizability[9] by Quinet and Champagne partially rectified this situation. Still, as their approach requires solving response equations for all geometrical perturbations, and because it is formulated in the molecular orbital basis, the size of the molecules that can be studied remains limited.

Bishop, Hasan, and Kirtman later introduced a scheme in which the geometry of the molecule was allowed to relax in the presence of applied static electric fields.[10] By calculating the hyperpolarizabilities at these different optimized geometries, the vibrational contributions to the hyperpolarizabilities, including also some of the anharmonic corrections as well as the zero-point vibrational corrections, could be determined without explicitly determining the molecular force constants, leading in principle to computational savings. However, the need to determine finite difference results from different geometries optimized in the presence of different finite electric fields, made the approach susceptible to numerical instabilities. Furthermore, the infinite optical frequency approximation[11] has to be applied in order to calculate the required pure vibrational contributions, although this restriction was later lifted at the price of added computational complexity.[12]

Luis et al. later introduced an approach involving electric field-relaxed coordinates.[13] In this approach, a set of field-induced coordinates were introduced, making the calculation of the pure vibrational contributions only dependent on the definition of a limited number of these field-induced coordinates. The number of field-induced coordinates are independent of the

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size of the molecule and only depends on the process being studied and the extent to which anharmonic corrections are included.

In this work we will use the perturbation theory approach of Bishop and Kirtman, calculating the necessary (hyper)polarizability derivatives using analytic techniques. We recently presented an atomic orbital-based scheme for calculating response functions of arbitrary order for time- and perturbation-dependent basis sets.[14] In this formalism, we can calculate the geometrical (hyper)polarizability derivatives using the $n + 1$ rule. We therefore have to determine third-order perturbed density matrices with respect to the applied electric fields. However, as there is a fixed and limited number of third-order perturbed density matrices, independent of the size of the molecule, this allows for calculations of pure vibrational contributions in large molecules. Nevertheless, we will still need to calculate the perturbed densities with respect to geometrical distortions in order to determine the molecular force field, and if both the force field and the (hyper)polarizability gradient are determined at the same level of theory, it is advantageous to use the geometry-perturbed density matrices as far as possible by applying the $2n + 1$ rule. Both approaches are implemented in our code,[14,15] but as we are going to use different approximations for the force field and the (hyper)polarizability gradients, the $n + 1$ rule will be used in this work. The formalism is also integrated with a linearly scaling energy[16] and response solver,[17] allowing us to study pure vibrational contributions of large molecules using basis sets of good quality.

There has been a recent study of the pure vibrational contributions of large donor−acceptor polyene-like systems.[18] It was demonstrated in this work that the pure vibrational contributions are very significant in comparison to the electronic contributions. However, small basis sets have been used and, in order to facilitate the comparison with experiment, primarily the contributions to the longitudinal component of the hyperpolarizability arising from the dominant in-chain vibrational modes were discussed. In this work we will therefore investigate the validity of this approximation by calculating the pure vibrational contributions to the hyperpolarizabilties of these molecules, including all vibrational modes in the molecules, and we will explore the importance of the choice of the basis set for such calculations. Although electron correlation effects have been demonstrated to be important for the calculation of pure vibrational contributions,[19−23] we will limit ourselves to calculations of the (hyper)polarizability derivatives at the Hartree−Fock level of theory. We will concentrate on the pure vibrational contributions to the studied polarizabilities, α^{v}, β^{v}, and γ^{v}, but we will nevertheless also report the corresponding electronic contributions, α^{e}, β^{e} and γ^{e}.

The remainder of the paper is organized as follows: in section II we will give a brief outline of the theory for pure vibrational contributions to (hyper)polarizabilities in the perturbation theory approach, as well as give an outline of our approach for calculating the necessary geometrical derivatives of the (hyper)polarizabilities in an atomic orbital-driven scheme. In section III we summarize the computational details of the calculations presented in section IV. In sectionV we give some concluding remarks and an outlook.

II. Theory

For completeness, we will here briefly introduce the perturbation theory approach for the calculation of pure vibrational corrections to nonlinear optical properties developed by Bishop and Kirtman.[6,7] The goal is here not to provide a full overview of this method, but instead highlight the essential features of the methodology, focusing on the terms which we will consider in this work. Following the discussion of the pure vibrational contributions to the second hyperpolarizability, we will briefly outline our approach for analytic calculations of the geometry derivatives of the (hyper)polarizabilities that determine the pure vibrational corrections to the nonlinear optical properties.

A. Pure Vibrational Corrections. In the sum-over-states expressions for the (hyper)polarizabilities, the summations run in principle over the vibronic states of the molecule and can in the case of the polarizability be written as

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \sum \mathscr{P}_{-\sigma,1} \sum_{k,K\neq 0,0} \frac{\langle 0,0|\hat{\mu}_\alpha|k,K\rangle\langle k,K|\hat{\mu}_\beta|0,0\rangle}{\omega_{kK,00} - \omega_\sigma} \tag{1}$$

where k is used to denote an electronic state and K the vibrational states. $\mathscr{P}_{-\sigma,1}$ permutes the dipole moment operator components and their associated frequencies ($\hat{\mu}_\alpha$, $\omega_{-\sigma}$) and ($\hat{\mu}_\beta$, ω_1). Atomic units have been used in the above equations and will be used throughout this paper. Assuming the Born−Oppenheimer approximation,[24,25] in which the vibronic wave function can be written as a product of a nuclear wave function C_K^N and an electronic wave function ψ_k^{el} which depends parametrically on the nuclear positions

$$\Psi_{k,K}(\mathbf{R},\mathbf{r}) = C_K^N(\mathbf{R})\psi_k^{\mathrm{el}}(\mathbf{r},\mathbf{R}) \tag{2}$$

we may divide the summation in eq 1 into a term in which the summation only runs over the vibrational manifold of the electronic ground state, and a term in which the summation involves all the electronic excited states

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \sum \mathscr{P}_{-\sigma,1}\left[\sum_{K\neq 0} \frac{\langle 0,0|\hat{\mu}_\alpha|0,K\rangle\langle 0,K|\hat{\mu}_\beta|0,0\rangle}{\omega_{0K,00} - \omega_\sigma} + \sum_{k\neq 0}\left\{\frac{\langle 0,0|\hat{\mu}_\alpha|k\rangle\langle k|\hat{\mu}_\beta|0,0\rangle}{\omega_{k,0} - \omega_\sigma}\right\}\right] \tag{3}$$

where we have introduced the completeness of the vibrational manifold for the electronic excited states, so that $\sum_K|K\rangle\langle K| = 1$, and where we have made the approximation $\omega_{kK,00} \approx \omega_{k,0}$. The first term in this equation is conventionally referred to as the pure vibrational contribution to the polarizability, and this is the term that will be the focus of the present work. The second term corresponds to the zero-point vibrationally averaged electronic polarizability.

A perturbation-theory approach for the calculation of these corrections has been developed by Bishop and Kirtman,[6,7] and this will be the basis for our calculations of the pure vibrational contributions. In this approach, the zeroth-order vibrational wave functions are represented as products of standard harmonic-oscillator wave functions for each of the normal modes of the molecule. Although corrections to the pure vibrational contributions arise both from mechanical anharmonicities (arising from the contributions from the force field beyond second order) and from electric anharmonicities (due to contributions from the geometry dependence of the electric properties beyond linear terms), and can in many cases be significant (see for instance ref 20), we will in this work assume that these anharmonic corrections are less important and can be ignored. This assumption is primarily motivated by the size of the molecules involved, making a full calculation including also anharmonic corrections practically impossible. As such, the results reported in the present paper will be obtained within the so-called double-harmonic approximation. We also note that anharmonic corrections may to a large extent cancel each other for some of the molecules studied here (see, e.g., the results previously reported for hexatriene[13]).

In order to calculate the properties of interest, the geometry dependence of the electric properties is expanded in a Taylor series with respect to the nuclear displacements. Since the electronic contribution to the electric properties at the reference geometry does not contribute to the pure vibrational contributions (since all integrals involving different vibrational states would vanish), the leading order contributions arise from the terms linear in the nuclear displacements. Combining this linear geometry dependence with the harmonic approximation for the vibrational wave function, we obtain the double-harmonic approximation in which electrical and mechanical anharmonicities are neglected.

In the notation of refs 6, 7, and 11, the contributions to the polarizability α, the first β, and second γ hyperpolarizabilities can in the double-harmonic approximation be written

$$\alpha^v = [\mu^2]^{(0,0)} \tag{4}$$

$$\beta^v = [\mu\alpha]^{(0,0)} \tag{5}$$

$$\gamma^v = [\alpha^2]^{(0,0)} + [\mu\beta]^{(0,0)} \tag{6}$$

where the superscripts specify the order of mechanical and electrical anharmonicities, repectively, and we shall omit them in the following. Moreover, since we shall evaluate only the static hyperpolarizabilities, we shall not specify the (zero) frequencies.

The explicit expressions for the terms in the above equations are given by[7]

$$[\mu^2]_{\alpha\beta} = \frac{1}{2}\sum \mathscr{P}_{-\sigma,1}\sum_{\mathrm{v}} \frac{\partial \mu_\alpha}{\partial Q_\mathrm{v}}\frac{\partial \mu_\beta}{\partial Q_\mathrm{v}}\lambda_\mathrm{v}^{\pm\sigma} \tag{7}$$

$$[\mu\alpha]_{\alpha\beta\gamma} = \frac{1}{2}\sum \mathscr{P}_{-\sigma,1,2}\sum_{\mathrm{v}} \frac{\partial \mu_\alpha}{\partial Q_\mathrm{v}}\frac{\partial \alpha_{\beta\gamma}}{\partial Q_\mathrm{v}}\lambda_\mathrm{v}^{\pm\sigma} \tag{8}$$

$$[\mu\beta]_{\alpha\beta\gamma\delta} = \frac{1}{6}\sum \mathscr{P}_{-\sigma,1,2,3}\sum_{\mathrm{v}} \frac{\partial \mu_\alpha}{\partial Q_\mathrm{v}}\frac{\partial \beta_{\beta\gamma\delta}}{\partial Q_\mathrm{v}}\lambda_\mathrm{v}^{\pm\sigma} \tag{9}$$

$$[\alpha^2]_{\alpha\beta\gamma\delta} = \frac{1}{8}\sum \mathscr{P}_{-\sigma,1,2,3}\sum_{\mathrm{v}} \frac{\partial \alpha_{\alpha\beta}}{\partial Q_\mathrm{v}}\frac{\partial \alpha_{\gamma\delta}}{\partial Q_\mathrm{v}}\lambda_\mathrm{v}^{\pm 23} \tag{10}$$

where Q_v denotes a normal mode, and the frequency term is defined as

$$\lambda_\mathrm{v}^{\pm\sigma} = \frac{1}{\omega_\mathrm{v} + \omega_\sigma} + \frac{1}{\omega_\mathrm{v} - \omega_\sigma} \tag{11}$$

We thus note that the critical quantities needed in order to calculate the pure vibrational corrections to the (hyper)polarizabilities are (1) the vibrational force field in order to determine ω_v, and (2) the geometrical first derivatives of the dipole moment and (hyper)polarizabilities, and we will in the next subsection describe our approach for calculating these geometrical derivatives of the (hyper)polarizabilities.

We note at this point that an analytic procedure for calculating geometrical derivatives of polarizabilities and hyperpolarizabilities has been presented by Quinet and Champagne.[8,9] Our approach differs from their approach in that it is developed fully in the atomic orbital basis and uses the $n + 1$ rule instead of the $2n + 1$ rule in order to avoid the computation of perturbed densities with respect to the geometrical distortions (vide infra). Given that an affordable and accurate vibrational force field is available, our approach is thus in principle more directly applicable to large molecular systems but provides otherwise the same functionality as that provided by the work of Quinet and Champagne.[89]

B. (Hyper)polarizability Gradients. In the following, we briefly outline the key elements of our approach for calculating the (hyper)polarizability gradients. The details of the formalism have been described elsewhere,[14] as well as in a recent paper concerned with coherent anti-Stokes Raman scattering (CARS),[15] and we will therefore be brief in the derivation of the geometrical derivatives of the dipole moment, the polarizability, and the first hyperpolarizability gradient. We do not discuss the calculation of the electronic contribution to the (hyper)polarizabilities, as these can be obtained from well-established response theory formulations,[26−34] although we use an AO-based quasi-energy formalism also for these quantities, following refs 14 and 17.

The starting point for deriving the (hyper)polarizability gradients is the generalized gradient formula[14]

$$Q^g = \frac{\mathrm{d}}{\mathrm{d}g}Q \overset{\mathrm{Tr}_t}{=} \frac{\partial}{\partial g}E(\mathbf{D}) - \mathbf{S}^g\mathbf{W} \tag{12}$$

where Q in our case is the Hartree−Fock quasi-energy (not to be confused with the normal mode Q_v introduced in eq 7), Q^g its derivative with respect to a nuclear displacement parameter g (perturbation strength), which makes a (generally) time-dependent perturbation of both the Hamiltonian and the AO basis, $E(\mathbf{D})$ the generalized Hartree−Fock energy, $\mathbf{S}^g = (\mathrm{d}/\mathrm{d}g)\mathbf{S}$ the geometry-derivative overlap matrix, and $\mathbf{W}$ the generalized energy-weighted density matrix (vide infra). Tr_t is here used to denote that we will take the trace of all matrix quantities and perform a time average. We note the close similarity between the expression for the quasi-energy gradient in eq 12 and that previously derived by Pulay for the conventional molecular geometrical gradient.[35] However, eq 12 is valid for a general time-dependent system expressed in a time- and perturbation-dependent atomic orbital basis.[14]

The generalized Hartree−Fock energy $E(\mathbf{D})$ in eq 12 contains an additional matrix $\mathbf{T}$ arising from the time dependence of the AOs, and we furthermore define the generalized Fock matrix $\mathbf{F}$ as the partial derivative (transposed) of $E(\mathbf{D})$

$$T_{\mu\nu} = \langle \chi_\mu | \dot{\chi}_\nu \rangle - \langle \dot{\chi}_\mu | \chi_\nu \rangle, \quad \dot{\chi}_\mu = \frac{\mathrm{d}}{\mathrm{d}t}\chi_\mu \tag{13}$$

$$E(\mathbf{D}) \overset{\mathrm{Tr}}{=} h_\mathrm{nuc} + v_\mathrm{nuc} + \left(\mathbf{h} + \mathbf{V} - \frac{i}{2}\mathbf{T}\right)\mathbf{D} + \frac{1}{2}\mathbf{G}(\mathbf{D})\mathbf{D} \tag{14}$$

$$\mathbf{F} = \frac{\partial}{\partial \mathbf{D}^T}E(\mathbf{D}) = \mathbf{h} + \mathbf{V} - \frac{i}{2}\mathbf{T} + \mathbf{G}(\mathbf{D}) \tag{15}$$

where h_nuc is the nuclear repulsion energy, v_nuc the potential energy between the nuclei and the external fields, $\mathbf{h}$ the integral matrix of the one-electron Hamiltonian, $\mathbf{V}$ the integral matrix of the electron-field interaction, and $\mathbf{G}$ the two-electron integral operator (Coulomb and exchange). Since $(i/2)\mathbf{T}$ is a Hermitian matrix, $E(\mathbf{D})$ is a real-valued function of time. For the unperturbed system (static, no fields), $\mathbf{T}$, $\mathbf{V}$, and v_nuc are zero.

The generalized energy-weighted density matrix $\mathbf{W}$ contains the generalized Fock matrix in addition to two terms arising from the time dependence of the density matrix

$$\mathbf{W} = \mathbf{DFD} + \frac{i}{2}\dot{\mathbf{D}}\mathbf{SD} - \frac{i}{2}\mathbf{DS}\dot{\mathbf{D}}, \quad \dot{\mathbf{D}} = \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{D} \tag{16}$$

We note that although we in this work only calculate the static gradient ($\omega_g = 0$, $T^g = 0$) induced by static electric fields, eqs

12, 14, and 16 could in principle be used to calculate frequency-dependent gradients induced by frequency-dependent fields.

The (homogeneous) electric field enters the potential operator as the negative dot product of the electric field vector $\boldsymbol{F}$ and the electric dipole operator $\hat{\mu}$

$$\hat{V}^t = -\boldsymbol{F} \cdot \hat{\mu}, \quad \hat{\mu} = -\sum_i \mathbf{r}_i + \sum_K Z_K \mathbf{R}_K \tag{17}$$

where Z_K is the charge of nucleus K, and v_{nuc} and $\mathbf{V}$ are therefore given by

$$v_{\mathrm{nuc}} = -\boldsymbol{F} \cdot \left(\sum_K Z_K \mathbf{R}_K\right), \quad V_{\mu\nu} = \boldsymbol{F} \cdot \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle \tag{18}$$

An oscillating electric field composed of several frequencies (ω_a, ω_b, ω_c) can be written as

$$\boldsymbol{F} = \boldsymbol{a} \exp(-i\omega_a t) + \boldsymbol{b} \exp(-i\omega_b t) + \boldsymbol{c} \exp(-i\omega_c t) + \boldsymbol{a}^* \exp(i\omega_a t) + \boldsymbol{b}^* \exp(i\omega_b t) + \boldsymbol{c}^* \exp(i\omega_c t) \tag{19}$$

where $\boldsymbol{a}, \boldsymbol{b}$, and $\boldsymbol{c}$ are complex strength vectors defining the intensity, phase, and polarization of the corresponding frequency component, which are all initially zero, thus corresponding to the unperturbed system. A static field component is obtained with a zero frequency, in which case the strength must be real-valued and the conjugated term can be omitted.

We can now obtain an expression for the (negative) electric dipole gradient by inserting eq 14 into eq 12, setting $\omega_g = 0$, and differentiating Q^g with respect to the field strength $\boldsymbol{a}$ of frequency $\omega_a = 0$

$$Q^g \overset{\mathrm{Tr}_t}{=} h^g_{\mathrm{nuc}} + v^g_{\mathrm{nuc}} + (\mathbf{h}^g + \mathbf{V}^g)\mathbf{D} + \frac{1}{2}\mathbf{G}^g(\mathbf{D})\mathbf{D} - \mathbf{S}^g\mathbf{W} \tag{20}$$

$$Q^{ga} = \frac{\mathrm{d}}{\mathrm{d}a} Q^g \overset{\mathrm{Tr}_t}{=} v^{ga}_{\mathrm{nuc}} + \mathbf{V}^{ga}\mathbf{D} + \mathbf{h}^g\mathbf{D}^a + \mathbf{G}^g(\mathbf{D})\mathbf{D}^a - \mathbf{S}^g\mathbf{W}^a \tag{21}$$

where we have used that for $\omega_g = 0$, the matrix $\mathbf{T}^g$ is zero, and that only v_{nuc} and $\mathbf{V}$ depend on $\boldsymbol{a}$, and not h_{nuc}, $\mathbf{h}$, $\mathbf{G}$, or $\mathbf{S}$, and that $\mathbf{G}^g(\mathbf{D}^a)\mathbf{D} = \mathbf{G}^g(\mathbf{D})\mathbf{D}^a$ when we take the trace of the resulting matrix products. In Q^{ga} we have omitted the contribution $\mathbf{V}^g\mathbf{D}^a$, since $\mathbf{V}$ is zero when $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c} = 0$. We will, however, include this contribution when differentiating Q^{ga} further below.

The contraction of the one-electron integrals $\mathbf{V}^{ga}$ and $\mathbf{h}^g$, and the two-electron integrals $\mathbf{G}^g$ with perturbed density matrices of different orders is straightforwardly achieved, as described in ref 15. We also refer to this work for the detailed expressions for the differentiated energy-weighted density matrix $\mathbf{W}$. The derivation of the linear set of equations that needs to be solved in order to determine the first-order perturbed density matrix has been given previously,[14,15] and these can be solved using for instance the linearly scaling response solver of Coriani et al.,[17] as done in the present work.

In a similar manner, using $\mathbf{b}$ to denote the second electric field strength with $\omega_b = -\omega_a$, we can derive the expression for the (negative) frequency-dependent polarizability gradient, which becomes

$$Q^{gab} \overset{Tr_t}{=} \mathbf{V}^{gb}\mathbf{D}^a + \mathbf{V}^{ga}\mathbf{D}^b + \mathbf{h}^g\mathbf{D}^{ab} + \mathbf{G}^g(\mathbf{D}^b)\mathbf{D}^a + \mathbf{G}^g(\mathbf{D})\mathbf{D}^{ab} - \mathbf{S}^g\mathbf{W}^{ab} \tag{22}$$

where we now have also utilized that the electric field only appears linearly in the Hamiltonian (in v_{nuc} and $\mathbf{V}$).

Further differentiation of the polarizability gradient with respect to a third electric field strength c, gives us the final expression for the (negative) gradient of the first hyperpolarizability tensor

$$Q^{gabc} \overset{\mathrm{Tr}_t}{=} \mathbf{V}^{ga}\mathbf{D}^{bc} + \mathbf{V}^{gb}\mathbf{D}^{ac} + \mathbf{V}^{gc}\mathbf{D}^{ab} + \mathbf{h}^g\mathbf{D}^{abc} + \mathbf{G}^g(\mathbf{D})\mathbf{D}^{abc} + \mathbf{G}^g(\mathbf{D}^{bc})\mathbf{D}^a + \mathbf{G}^g(\mathbf{D}^b)\mathbf{D}^{ac} + \mathbf{G}^g(\mathbf{D}^c)\mathbf{D}^{ab} - \mathbf{S}^g\mathbf{W}^{abc} \tag{23}$$

The response equations are solved only for the external electric field perturbations, but the above equations then require that we determine the electric-field perturbed density matrix to third order, $\mathbf{D}^{abc}$. However, in this way the computational effort of the vibrational contribution is of the same order as that of the electronic contribution. This enables calculations for large polyatomic systems with many degrees of freedom. For a nonlinear molecule consisting of N atoms, there are $3N - 6$ response equations to be solved if one applies the geometry-perturbed wave functions (if, for instance, one uses the $2n + 1$ rule), whereas there are only three response equations for the first-order perturbation corrections to the dipole moment, six for the second-order, and 10 for the third-order perturbation corrections. We use this fact in order to obtain the β^{v} and γ^{v} static hyperpolarizabilities solving only a limited number (19) of response equations. If, in contrast, we attempted to take advantage of the $2n + 1$ rule and to utilize only the second-order perturbation corrections, the calculations for the largest molecule studied in this work would require solving approximately 200 response equations. We refer to ref 14 for details on our iterative scheme for determining higher-order perturbed density matrices using the linear-scaling response solver of Coriani et al.[17]

III. Computational Details

The procedure leading to the vibrational hyperpolarizabilities can be clearly partitioned into two steps—the first being the derivation of the force fields, the second the analysis of the electric-field perturbation parameters. There is no formal requirement that both steps of the calculation should be done at the same level of approximation—in fact, experimental data have been often used for the force fields in earlier theoretical work.[36] We shall, however, calculate all the necessary quantities, but we nevertheless take advantage of this degree of freedom and use different approximations for the force field compared to the computational methods used to determine the polarizabilities and their geometrical derivatives.

In the geometry optimization we use the DFT/B3LYP approach.[37−39] This approximation is also used to determine the final Hessian and thus the force field required to calculate the vibrational polarizabilities. The superiority of DFT relative to the Hartree−Fock approximation in determining molecular geometries, harmonic frequencies, and force constants is well established.[40] Furthermore, there is little computational overhead involved in the B3LYP approach relative to Hartree−Fock. On the other hand, in the calculation of the electric properties we will systematically use the Hartree−Fock approach, since our implementation of geometrical derivatives of the hyperpolarizabilities currently is limited to Hartree−Fock wave functions. However, we note that theoretical studies have demonstrated that the differences between the dipole and polarizability vibrational transition moments computed in the two approaches are not very significant.[41] Furthermore, the B3LYP functional is known to have deficiences in treating charge-transfer excited states,[42−44] which can be expected to be important for the nonlinear optical properties of the push−pull systems studied in this work, potentially making the Hartree–Fock approach more qualitatively correct than the B3LYP formalism. Still, the dependence of the calculated (hyper)polarizability derivatives on the choice of reference geometry and the level of theory needs to be studied in more detail, preferably applying state-of-the-art correlated ab initio methods. However, this is beyond the scope of the present study.

We use different basis sets at each stage of the calculation. We analyze the results obtained with the correlation-consistent basis sets of Dunning and co-workers[45,46] (denoted in the following as XZ, X = D, T, Q being the cardinal number of the basis), as well as with the related augmented (aXZ) and doubly augmented (dXZ) correlation-consistent basis sets.[47−49] In addition, we consider the Turbomole-TZV2P[50] and Sadlej's polarized basis sets, PolX[51] and Z3PolX.[52]

We shall not dicuss the individual tensor components of all the properties investigated in this paper. The results will be given only for the isotropic averages, defined by the equations

$$\alpha = \frac{1}{3}\alpha_{\eta\eta} \tag{24}$$

$$\beta_Z = \frac{1}{5}(\beta_{Z\eta\eta} + \beta_{\eta Z\eta} + \beta_{\eta\eta Z}) \tag{25}$$

$$\gamma = \frac{1}{15}(\gamma_{\xi\eta\eta\xi} + \gamma_{\xi\eta\xi\eta} + \gamma_{\xi\xi\eta\eta}) \tag{26}$$

where summation over repeated greek indices is implied and, for β_Z, the Z axis is determined by the direction of the dipole moment. These definitions are used both for the vibrational and electronic properties.

IV. Results and Discussion

We begin the discussion with an analysis of the results for the water molecule. For this molecule, we will consider the dependence of the computed properties on the choice of molecular geometry and we will describe in detail their convergence with respect to the extension of the basis set.

Next, we analyze the electronic and vibrational properties of three all-trans polyenes: hexatriene, C_6H_8; octatetraene, C_8H_{10}; and decapentaene, $C_{10}H_{12}$. The interpretation of the results is simplified by the high symmetry of these molecules—the dipole moment and first hyperpolarizability vanish by symmetry. Finally, we consider three 4-dimethylaminophenylpolyene aldehydes, $C_{11}H_{13}NO$; $C_{19}H_{23}NO$ and $C_{29}H_{35}NO$ (molecules 1′, 2′, and 4′ in ref 53 later denoted as IIIa, IIIb, and IIIc in ref 18). These aldehydes belong to a class of push–pull molecules with a donor and an acceptor group, linked by a polyenic chain which increases along this sequence of three molecules. The large values of the β_Z hyperpolarizability in these compounds are due to the delocalization of the π electrons in the chain.

In the discussion of the results for the polyenes and push–pull aldehydes, we shall repeatedly refer to the work by Castiglioni et al.[18] The authors discuss an interpretation of the vibrational contributions to first and second hyperpolarizabilities and report estimates of these properties extracted from experimental IR and Raman spectra. It should be kept in mind, however, that a series of approximations was needed in order to relate the experimental data to the β^v and γ^v hyperpolarizabilities. Furthermore, the experimental results are obtained in a solvent and for specific frequencies, whereas we will discuss static properties for isolated molecules.

A. Water. In order to analyze the geometry and basis set dependence of the results, we have studied the electronic and vibrational properties of the water molecule. The results reported in Table 1 were obtained for geometries optimized at the DFT/B3LYP level with the aug-cc-pVTZ and Turbomole-TZV2P basis sets, and using the corresponding Hessian determined within the same computational approach as in the geometry optimization.

For the Dunning basis sets, we observe that at least one set of diffuse functions is needed to obtain qualitatively correct results. Furthermore, the second set of diffuse functions is more important than an increase in the cardinal number X. Thus, to obtain at least qualitative accuracy we need the dDZ or the aTZ basis sets, and in order to obtain quantitative accuracy one should use the dTZ basis set rather than the aQZ basis set. The TZV2P basis set can be seen to be unsuitable for the calculation of the polarizabilities. In contrast, the small basis sets developed by Sadlej perform well, the results obtained being comparable to those obtained with the much larger basis sets by Dunning et al. In particular, the PolX basis set gives reliable results for both the electronic and vibrational polarizabilities. We also note that the [α^2] contribution to γ^v appears to be easier to describe, the strongest basis set dependence to γ^v coming from the [$\mu\beta$] term.

The values obtained for the two different geometries and associated force fields are very similar, with the results not differing by more than 2%. The differences are of the same order of magnitude for the vibrational and the electronic polarizabilities and do not depend significantly on the basis set chosen to study the properties. We shall therefore for the larger molecules report the results obtained for the geometries optimized with the much smaller Turbomole-TZV2P basis set, with the exception of the largest molecule for which we use the geometry and Hessian computed with the even smaller Turbomole-TZVP basis.

A detailed comparison with results reported in the literature is beyond the scope of this paper, as there are in general too many differences between our computational approach (in terms of choice of basis set, description of electron correlation and approach for calculating the pure vibrational contributions). We will therefore only make a qualitative comparison with some results published in the literature.

The electronic hyperpolarizabilities of H_2O have been the subject of several theoretical studies at different levels of theory. Maroulis studied the electronic hyperpolarizabilities of water using large basis sets,[54] and our dQZ results are in good agreement with his basis-set limit Hartree–Fock results.

In a study of the pure vibrational contributions to the hypermagnetizability of the water molecule, the pure vibrational contributions to the polarizability was also reported for a complete active space self-consistent field wave function (CASSCF),[55] using this level of approximation for both the dipole gradients and the force field. We would expect our force field to be of higher quality than the CASSCF force field, due to a better approximation for the dynamic electron correlation effects, whereas the dipole gradients in ref 55 includes electron correlation in contrast to our HF results. Our results for the pure vibrational contribution to the static polarizability are 0.149 au for α_{xx} and 0.967 for α_{zz} using the TZV2P geometry and Hessian, which are only in fair agreement with the results of ref 55 $\alpha_{xx} = 0.115$ and $\alpha_{zz} = 0.761$ au.

Luis et al.[56] calculated β^v at the SCF level, using the polarized basis set of Sadlej. For a proper comparison of the static β^v, we need to extract the double-harmonic approximation value from their results. This can be achieved (see, e.g., ref 57) using as the source number their infinite-frequency approximation Pockels effect $\beta^v(-\omega,\omega,0)$, which leads to a static $\beta^v = 7.035$

TABLE 1: Basis Set and Geometry Dependence of the H_2O Results[a]

	Electronic Properties							
	μ^e		α^e		β^e		γ^e	
TZV2P	0.80709	0.80803	6.8517	6.8439	−15.898	−15.851	203.28	202.63
DZ	0.80743	0.80828	5.0546	5.0479	−18.377	−18.338	122.58	122.18
TZ	0.79466	0.79561	6.6606	6.6531	−16.765	−16.719	160.87	160.35
QZ	0.78759	0.78856	7.4091	7.4002	−14.953	−14.910	235.72	235.07
aDZ	0.78418	0.78516	8.1952	8.1850	−10.552	−10.517	603.60	602.06
aTZ	0.77787	0.77885	8.4841	8.4732	−11.870	−11.828	740.90	739.09
aQZ	0.77703	0.77802	8.5655	8.5544	−11.388	−11.343	838.38	836.34
dDZ	0.77866	0.77966	8.5793	8.5680	−9.199	−9.157	907.81	905.65
dTZ	0.77762	0.77861	8.6023	8.5910	−11.013	−10.968	998.75	996.23
dQZ	0.77701	0.77800	8.6016	8.5903	−11.324	−11.278	999.60	997.02
PolX	0.77815	0.77913	8.5561	8.5448	−8.737	−8.690	854.94	852.89
Z3PolX	0.75568	0.75672	8.3848	8.3739	−9.345	−9.293	731.43	729.67

	Vibrational Properties			
	α^v		β^v	
TZV2P	0.3444	0.3388	15.300	15.176
DZ	0.3232	0.3180	16.332	16.190
TZ	0.3476	0.3420	14.440	14.318
QZ	0.3642	0.3584	12.875	12.813
aDZ	0.3687	0.3628	11.709	11.696
aTZ	0.3777	0.3716	10.327	10.347
aQZ	0.3777	0.3717	9.698	9.732
dDZ	0.3801	0.3740	9.234	9.279
dTZ	0.3777	0.3716	9.351	9.392
dQZ	0.3778	0.3717	9.392	9.433
PolX	0.3819	0.3758	9.514	9.557
Z3PolX	0.3821	0.3758	8.312	8.353

	γ^v and Its Two Contributions					
	γ^v		$[\alpha^2]$		$[\mu\beta]$	
TZV2P	116.35	115.24	164.89	163.43	−48.54	−48.20
DZ	108.28	107.29	162.42	160.94	−54.14	−53.66
TZ	107.25	106.11	150.96	149.57	−43.71	−43.46
QZ	112.13	111.07	154.76	153.43	−42.62	−42.36
aDZ	126.68	125.58	168.59	167.20	−41.91	−41.63
aTZ	136.80	135.51	168.38	166.95	−31.58	−31.44
aQZ	141.69	140.30	168.37	166.91	−26.68	−26.61
dDZ	142.06	140.61	167.36	165.90	−25.30	−25.28
dTZ	144.60	143.16	168.91	167.43	−24.30	−24.27
dQZ	146.08	144.60	168.81	167.34	−22.73	−22.74
PolX	136.47	135.10	166.37	164.91	−29.90	−29.82
Z3PolX	139.27	137.79	159.24	157.85	−19.97	−20.06

[a] For each property, the pair of numbers gives the values at aTZ geometry and Hessian (first) and TZV2P geometry and Hessian (second). The aTZ geometry has a bond distance of 0.962 10 Å and a bond angle of 105.08°, whereas the TZV2P geometry has a bond distance of 0.961 29 Å and a bond angle of 104.89°.

au. The use of different force fields explains the deviation between this result and the value we obtained applying the same Sadlej basis set for the polarizability derivatives, $\beta^v = 9.5$ au.

Our results for γ^v are only in qualitative agreement with the values obtained in the same approximation by Bishop and Dalskov,[11] 129.16 and −21.88 au for the $[\alpha^2]$ and $[\mu\beta]$ contributions, to be compared with approximately 166 and −30 au in our calculations. On the other hand, our results for the pure vibrational contribution to the mean second hyperpolarizability are smaller than the older values by Bishop et al.[58] which include also anharmonic corrections—150 au for the full SCF calculation, or 184 au when an MP2 force field was used.

B. Hexatriene, Octatetraene, and Decapentaene. To confirm that we can apply Sadlej's PolX basis set[51] for larger molecules, we have performed a series of additional test calculations for hexatriene. As shown in Table 2, the PolX results do not differ significantly from those obtained using the much larger Dunning basis sets, and we have therefore chosen this basis set for all the subsequent calculations on the large systems. In particular, considering the size of the different basis sets, it is obvious that for much larger molecules it would be very difficult to obtain results of similar quality with any of the other applied basis sets.

TABLE 2: Basis Set Dependence of the Hexatriene Results[a]

basis	CGTO	γ^e	γ^v
6-31G	70	10654	31387
6-31G*	100	9830	31705
Z3PolX	156	29941	43411
PolX	216	35015	44820
TZV2P	216	15294	39086
dDZ	296	35337	44739
aTZ	460	33050	45220

[a] The same geometry and Hessian (obtained at the DFT/B3LYP level with the TZV2P basis set) is used in all the calculations.

TABLE 3: Polarizabilities of C_6H_8, C_8H_{10}, and $C_{10}H_{12}$[a,b]

	C_6H_8	C_8H_{10}	$C_{10}H_{12}$
	Electronic Polarizabilities		
α^e	93.8	139.7	194.1
γ^e	35015	86202	199316
$\gamma^e_{ZZZZ}/5$	20659	68064	172612
	Vibrational Polarizabilities		
α^v	4.89	8.15	12.76
γ^v	44820	154479	436232
$[\alpha^2]$	42777	155911	447686
$[\mu\beta]$	2043	−1432	−11454
$\gamma^v_{ZZZZ}/5$	36171	140487	416868

[a] Sadlej basis set. [b] In the dominant component approximation $\gamma = 3/15\ \gamma_{ZZZZ}$. The Z axis is defined as the axis corresponding to the largest rotational constant.

The polarizabilities of hexatriene, octatetraene, and decapentaene are collected in Table 3. For these all-trans polyenes, the first hyperpolarizability is zero by symmetry. It has often been assumed that the second hyperpolarizability of these molecules is determined by the tensor component along the chain, $\gamma \approx \gamma_{ZZZZ}/5$. Comparing the isotropic value of the electronic hyperpolarizability with such an estimate, we find that this becomes a good approximation only for the largest molecule in the series, $C_{10}H_{12}$. This approximation gives almost 90% of the isotropic value of γ^e for $C_{10}H_{12}$, whereas for C_6H_8 and C_8H_{10} it only contributes about 60% and 80%, respectively, of the tensor average of the electronic second hyperpolarizability. This approximation is, however, much better for the vibrational hyperpolarizability, where the γ_{ZZZZ} component provides approximately 81%, 91% and 96% of the total γ^v for C_6H_8, C_8H_{10}, and $C_{10}H_{12}$, respectively.

For hexatriene, the longitudinal component of the pure vibrational contribution to the second hyperpolarizability has previously been computed using a set of field-induced coordinates (which also includes anharmonic terms in the expansion of γ^v).[13] The total RHF/6-31G result $\gamma^v_{ZZZZ} = 91\,400$ au, with the dominant contribution $[\alpha^2] = 89\,400$ au, is smaller than our 6-31G value $\gamma^v_{ZZZZ} = 134\,423$ au. Although many of the anharmonic corrections to the pure vibrational contributions were shown to be large, they largely cancel each other, making the overall anharmonic correction a modest 4%. The large differences compared to the results of ref 13 is therefore due to the different choices of force field and equilibrium geometries. These effects are seen to be substantial, increasing the vibrational hyperpolarizability of ref 13 by almost 50%. Although not numerically significant, we note that our force field leads to a positive contribution from $[\mu\beta]$, whereas the results in ref 13 for this term are negative. The force field is thus clearly important in order to determine the pure vibrational contribution.

By symmetry, each vibrational mode leads in these molecules to either an $[\alpha^2]$ or a $[\mu\beta]$ contribution. In the total γ^v, the $[\alpha^2]$ contribution is dominant, and the role of $[\mu\beta]$ is practically negligible (for all the polyenes, it contributes less than 5% to the total γ^v). As shown by Champagne et al.,[59] there are two dominant modes contributing to γ^v; we find the $[\alpha^2]$ contribution of the first to be 24 480, 90 684, and 262 490 au for C_6H_8, C_8H_{10}, and $C_{10}H_{12}$, and the contribution of the second mode is 8224, 39 541, and 134 049 au, respectively. Their role is increasing with increasing chain length, and together they contribute 90% of the total γ^v for $C_{10}H_{12}$. For decapentaene, the contribution of the second mode is 10 times larger than that of the third contributing mode. The role of the first mode is decreasing, whereas the role of the second mode is increasing with increasing chain length.

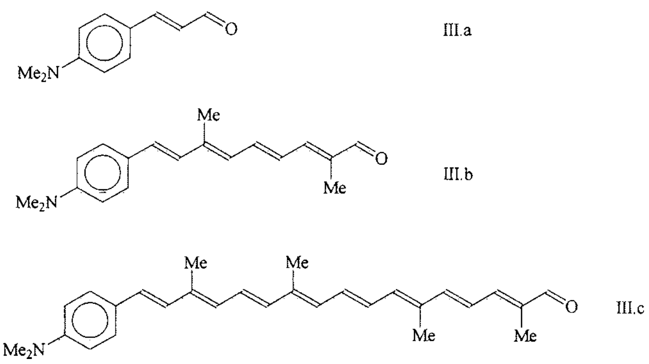

Figure 1. Molecular structure of the three push−pull aldehydes studied in this work, together with their corresponding symbols. See also Figure 1 in ref 18.

As discussed by Castiglioni et al.,[18] in chain-like molecules with delocalized π electrons the dominant modes for the vibrational contribution can be described by analyzing the sum over all the pairs of adjacent single and double bonds of the terms $R^{C-C} - R^{C=C}$.[18] These modes represent the oscillating degree of bond alternation of the chain and dominate the Raman spectrum. Our results confirm this interpretation. For instance, the frequencies of the two dominant modes are 1686.88 and 1221.55 cm^{-1} in C_6H_8, 1663.87 and 1214.49 cm $^{-1}$ in C_8H_{10}, and 1642.19 and 1207.65 cm $^{-1}$ in $C_{10}H_{12}$, while the experimental frequencies of the two most intense Raman bands, given by Castiglioni et al.,[18] are 1626 and 1191 cm $^{-1}$ in C_6H_8 and 1613 and 1179 cm $^{-1}$ in C_8H_{10}. Moreover, for all the dienes, the atomic displacements in these two modes are indeed related to changes in the R^{C-C} and $R^{C=C}$ distances (see the discussion of the modes involving the effective conjugation coordinate and hydrogen wagging in ref 59).

The electronic and vibrational hyperpolarizabilities estimated from experimental data and obtained at the RHF/6-31G* level in ref 18 are systematically smaller (approximately by a factor of 2) than our results. Since we use a presumably more reliable DFT force field and a larger basis set, our ab initio values should in principle be more accurate for isolated polyene molecules.

C. Push−Pull Aldehydes. The push−pull aldehydes, with electron donor and acceptor groups at the ends, represent a class of molecules with large first hyperpolarizabilities. The molecules studied in this work are shown in Figure 1. For the electronic contribution, the large values of β can be attributed to the existence of a low-lying charge-transfer state possessing a large oscillator strength.[53] For the vibrational contribution, the dominant effect is similar to that discussed for all-trans polyenes, corresponding to single/double bond alternation in the chain.

The results for IIIa, IIIb, and IIIc are collected in Table 4. The approximation of the isotropic value as $\beta = 3\beta_{ZZZ}/5$ is excellent for the electronic properties and for the vibrational properties of IIIb and IIIc, the error being less than 1%. On the other hand, γ differs more noticeably from $\gamma_{ZZZZ}/5$; in this case the error is closer to 10% for both the electronic and vibrational hyperpolarizabilities.

The analysis of the individual mode contributions for the push−pull aldehydes is more complicated than for the polyenes. There are both positive and negative contributions to β^v and γ^v, and both the $[\alpha^2]$ and $[\mu\beta]$ terms are relevant (similar effects have been observed in the studies of other π-conjugated push−pull molecules, see, e.g., ref 60). Moreover, the contributions of numerous vibrational modes are of similar magnitude. Although the oscillations of the carbon atoms in the chain are

TABLE 4: Polarizabilities of Push-Pull Aldehydes, $C_{11}H_{13}NO$, $C_{19}H_{23}NO$, and $C_{29}H_{35}NO$ (IIIa, IIIb, and IIIc)[a,b]

	IIIa	IIIb	IIIc
	Electronic Polarizabilities		
μ^e	3.22048	3.79389	4.21021
α^e	163.1	363.5	713.2
β^e	1574	7802	23000
$3\beta_{ZZZ}/5$	1583	7812	23045
γ^e	7.688×10^4	76.56×10^4	489.0×10^4
$\gamma^e_{ZZZZ}/5$	5.334×10^4	70.93×10^4	479.5×10^4
	Vibrational Polarizabilities		
α^v	61.3	108.6	192.2
β^v	5284	32251	103154
$3\beta^v_{ZZZ}/5$	4532	31094	103173
γ^v	12.62×10^4	278.6×10^4	2117×10^4
$\gamma^v_{ZZZZ}/5$	13.76×10^4	262.8×10^4	1938×10^4

[a] Sadlej basis set. [b] In the dominant component approximations: $\beta_{\|} = (3/5)\beta_{ZZZ}$ and $\gamma = (3/15)\gamma_{ZZZZ}$. The dipole moment is along the Z axis.

important, the displacements of other heavy atoms also contribute to these modes and the overall picture is not as clearcut as for the all-trans polyenes.

In the comparison of experimental and theoretical properties in ref 18, RHF/3-21G values were used. To estimate the role of the basis set, we have therefore repeated our calculations for the IIIb molecule using the same DFT force field as above, but employing the 3-21G basis set in the hyperpolarizability calculations. We obtain for β^v_{ZZZ} and γ^v_{ZZZZ} approximately 75% of the values obtained with the PolX basis, and our 3-21G results for IIIb are thus qualitatively correct (the agreement is even somewhat better for the electronic properties). The electronic contributions to the first hyperpolarizability given by Castiglioni et al.[18] are of the same order of magnitude as ours. On the other hand, their RHF/3-21G values of β^v_{ZZZ} (which are similar to those estimated from experimental data) are significantly different—smaller by a factor of 4—from our results shown in Table 4. Presumably, this difference is due to the use of a RHF/3-21G force field in ref 18, clearly demonstrating the importance of the force field in the determination of pure vibrational contributions to nonlinear optical properties.

V. Conclusions

We have presented an analytic scheme for the efficient calculation of pure vibrational contributions to the hyperpolarizabilities of large molecules. The approach uses the elements of the density matrix in the atomic orbital basis as the basic variables, allowing recent advances in linear-scaling response theory to be utilized. By calculating perturbed densities up to third order for the applied electric field, only 19 response equations need to be solved in order to calculate the pure vibrational contributions to the second hyperpolarizability, independent of the size of the molecule.

Using the analytic approach presented in this paper, we have demonstrated that the vibrational contributions to the polarizabilities can be calculated efficiently. Indeed, if it is possible to optimize the molecular geometry and determine the force field, the calculation of first and second hyperpolarizability tensors can easily be undertaken, as the computational costs are lower than the costs connected with the determination of the molecular force field, at least in terms of the number of response equations that need to be solved. The use of a perturbation-theory approach for the calculation of the pure vibrational contributions allows us to use different approximations for the force field and the (hyper)polarizability derivatives, and we have taken advantage of this fact to use different approaches and different basis sets for determining the different properties entering the expressions for the pure vibrational contributions. In particular, small basis sets specifically optimized for the study of molecular electric properties were applied in the analysis of the polarizabilities.

The results indicate that for molecules that contain conjugated polyene chains, the role of the pure vibrational contribution to the hyperpolarizability becomes dominant with increasing chain length, being in these cases much larger than the electronic counterpart. It appears that for long polyene chains, simple calculations, in which only the dominant tensor component is studied or in which relatively small basis sets are used, may be quite successful in the sense that these simple approximations give a qualitatively correct description of the properties, and the results become more accurate with increasing chain length. However, there are two factors that may be essential and limit such a simple approach: the geometry and the force field should be accurately determined and the basis sets, although small, should be designed to properly describe the applied perturbations.

We believe that the present scheme for calculating higher-order molecular properties, using an atomic orbital-based scheme and requiring only a limited number of response equations to be solved, in combination with linear-scaling technology, opens new possibilities for the study of pure vibrational contributions to nonlinear optical properties. Work is in progress in order to extend the implementation to also include electron correlation effects in the form of density-functional theory, as well as the calculation of geometrical second derivatives of the electronic hyperpolarizabilities, which will enable us to perform analytic calculations also of the zero-point vibrational contributions as well as anharmonic contributions to the pure vibrational contributions of the nonlinear optical properties.

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