Automated calculation of anharmonic vibrational contributions to first hyperpolarizabilities: Quadratic response functions from vibrational configuration interaction wave functions

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Quadratic response functions are derived and implemented for a vibrational configuration interaction state. Combined electronic and vibrational quadratic response functions are derived using Born–Oppenheimer vibronic product wave functions. Computational tractable expressions are derived for determining the total quadratic response contribution as a sum of contributions involving both electronic and vibrational linear and quadratic response functions. In the general frequency-dependent case this includes a new and more troublesome type of electronic linear response function. Pilot calculations for the FH, H_2O, CH_2O, and pyrrole molecules demonstrate the importance of vibrational contributions for accurate comparison to experiment and that the vibrational contributions in some cases can be very large. The calculation of transition properties between vibrational states is combined with sum-over-states expressions for analysis purposes. On the basis of this some simple analysis methods are suggested. Also, a preliminary study of the effect of finite lifetimes on quadratic response functions is presented. © *2009 American Institute of Physics*. [doi:10.1063/1.3246349]

I. INTRODUCTION

A tremendous amount of research is directed at discovering new materials with special nonlinear optical (NLO) properties due to their potential use in, e.g., optical storage media; see for example Ref. 1 for a recent review. Theoretical descriptions of NLO properties have similarly received a lot of attention as they represent challenging theoretical problems in electronic structure theory[2] as well as for the inclusion of vibrational contributions.[3,4]

It is a well-established fact that molecular properties depend on the motion of the nuclei and although such effects are often neglected in computational studies, they may certainly be important for high-accuracy studies where comparison to experiment is a central issue. The contributions to a molecular property of interest from the internal vibrational motion of the nuclei are divided in two: (i) vibrational averaging and (ii) the direct response of the nuclear motion to a perturbing electromagnetic field for (hyper)polarizabilities known as pure vibrational (PV) contributions.[3] Both effects apply for vibrational ground states as well as for excited vibrational states which become increasingly populated at finite temperatures. In the present work we report the theory and an implementation of a method that allows calculation of both PV and zero-point vibrational contributions (ZPVCs) in order to retrieve total molecular responses up to the first hyperpolarizability.

The calculation of molecular properties including contributions from both the electrons and the dynamics of the nuclei is not new, although still far from standard. Indeed this field has been pioneered for a number of years by Bishop and Kirtman, see Refs. 3 and 4. Following their work, several strategies for obtaining the PV and ZPVC terms discussed above have been developed. Recently, in particular the nuclear relaxation approach[5–8] has been pursued also in the context of anharmonic vibrational wave function formalisms[9,10] although most work has been based on vibrational perturbation theory. The nuclear relaxation approach allows for computations of several linear and NLO properties provided that at least one frequency is zero. Many studies have now established that the vibrational contributions are important, and that they can be very large, if not dominant, in the static limit.[11–16]

Response theory[17–19] is a well established approach for calculating electronic contributions to molecular properties. A simple perturbation theory approach provides working equations of sum-over-states (SOS) form but a truncation of the included states must be performed in practical calculations. To reach convergence is troublesome except for small systems. Within the formalism of response theory one explores, by construction, the full state space (within the given basis). Unlike in simple finite field approaches, response theory allows that all components of the electromagnetic radiation have nonzero frequencies. Furthermore, response

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theory can be used to accurately calculate excitation energies and corresponding transition moments for both ground to excited state transitions and between two excited states. Thus, a large variety of molecular properties can be calculated by response theory including NLO properties. This analytical response theory approach has been applied to electronic wave function theory and density functional theory (DFT) in many different contexts.[18,20–23] Quadratic response functions allow for the calculation of frequency-dependent first hyperpolarizabilities and, via the finite field approach, also for some second hyperpolarizabilities as, e.g., those relevant for the electric field induced second harmonic generation (SHG), where one of the frequencies is zero.

Response theory has primarily been restricted to electronic wave functions, but more recently the response terminology has also been introduced in the context of anharmonic vibrational wave functions.[24,25] In particular, a response theory approach to determine linear response functions within the vibrational configuration interaction (VCI) framework was developed.[25] One of the main results of this work is the derivation and implementation of quadratic response functions for the VCI wave function. The VCI method for calculating accurate vibrational energies and wave functions beyond the mean-field approximation has a long history. The reader is referred to recent reviews[26,27] for details and further references. The increasing speed of modern computers and the availability of fast, reliable, and accurate electronic structure program packages combined give a solid base for the generation of highly accurate anharmonic potentials. We are in this work using our previously reported implementations based on Taylor expansion[28] or a grid approach,[29] and we refer to these works[28,29] for further references on this aspect. The resulting potential energy (hyper-)surfaces (PESs) may be used to generate anharmonic vibrational wave functions. The corresponding property surfaces may be used to compute ZPVC to molecular properties, as well as higher order vibrational responses. In effect, the calculation of vibronic molecular properties is becoming more and more feasible with explicit anharmonic wave functions.

To put the use of the vibrational quadratic response function in context we begin with a simple but new derivation of the combined electronic and vibrational quadratic response function. In some sense the outset is similar to that of Bishop and Kirtman, which has been widely used, see, e.g., Refs. 3 and 4. Here, however we aim at identifying response functions in the expressions and in particular we find slightly different expressions—including a so-called mixed linear response function contribution—which only in the static limit are the same as the final results reported by Bishop and Kirtman. We explore the effect of the extra terms that so far have been neglected and discuss their problematic features. The final expressions allow for the calculation of the total electronic and vibrational response in conjunction with electronic linear and quadratic response functions and vibrational linear and quadratic response functions. However, an extended definition of linear response functions must be given.

The outline of the paper is as follows. After the theory in Sec. II, we give the computational details in Sec. III. Some sample calculations are reported and discussed in Sec. IV before we summarize the main results in Sec. V.

II. THEORY

A. General aspects

The time evolution of a molecular system is governed by the time-dependent Schrödinger equation

$$H|\bar{\Psi}_o(t)\rangle = i\frac{\partial}{\partial t}|\bar{\Psi}_o(t)\rangle, \tag{1}$$

where H is the Hamiltonian,

$$H = H_o + V^t. \tag{2}$$

H_o is the unperturbed Hamiltonian and V^t is a time-dependent perturbation operator of the form

$$V^t = \sum_y \epsilon_y(\omega_y) Y \exp(-i\omega_y t), \tag{3}$$

where Y is a perturbation operator with associate frequency ω_y. $\epsilon_y(\omega_y)$ is a perturbation strength parameter. We use atomic units throughout this paper.

Following general strategies and expanding the time-dependent expectation value of a Hermitian operator X in orders of the perturbation in Eq. (3), one obtains (see Ref. 19)

$$\begin{aligned}\langle\bar{\Psi}_o(t)|X|\bar{\Psi}_o(t)\rangle = \langle\Psi_o|X|\Psi_o\rangle &+ \sum_y \epsilon_y(\omega_y)\langle\langle X,Y\rangle\rangle_{\omega_y} \\ &\times\exp(-i\omega_y t) + \frac{1}{2}\sum_{y,z}\epsilon_y(\omega_y)\epsilon_z(\omega_z) \\ &\times\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}\exp(-i(\omega_y+\omega_z)t) \\ &+ \cdots,\end{aligned} \tag{4}$$

where $|\Psi_o\rangle$ represents the unperturbed wave function and with $\langle\langle X,Y\rangle\rangle_{\omega_y}$ and $\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}$ the linear and quadratic response functions, respectively. $\langle\Psi_o|X|\Psi_o\rangle$ is the usual expectation value.

At this point we note that the following analyses are general in the sense that the operators X, Y, Z, etc. may correspond to any perturbation operator. In this sense, we deviate from the previous combined electronic and vibrational treatments that traditionally consider directly the cases where the perturbation operators correspond to components of the dipole moment.[3,4,6,11] In this case one obtains expressions for the polarizability (α) and hyperpolarizabilities (β, γ). In the response function formalism, these quantities are readily obtainable as

$$\alpha_{ij}(\omega_y) = -\langle\langle\mu_i,\mu_j\rangle\rangle_{\omega_y}, \tag{5}$$

$$\beta_{ijk}(\omega_y,\omega_z) = -\langle\langle\mu_i,\mu_j,\mu_k\rangle\rangle_{\omega_y,\omega_z} \tag{6}$$

for the α_{ij} and β_{ijk} components of the polarizability and first hyperpolarizability, respectively.

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B. Separation of electronic and vibrational contributions

Following the Born–Oppenheimer approximation one may separate the motion of the nuclei and the electrons with the wave function assuming a simple product form. In general terms such an approach is standard. Following previous work,[25] we will write the vibronic states as $|K\rangle|k_K\rangle$, where $|K\rangle$ represents an electronic wave function and $|k_K\rangle$ represents the wave function of the kth vibrational level in the Kth electronic state. Only the effect of quantized vibration is considered for the nuclear motion, i.e., molecular rotation and translation are omitted.

We assume now that the vibrational energy differences are small compared with the electronic energy differences and that the external frequency is far from being in resonance with the electronic energies. This potentially allows the use of closure over the vibrational states in the excited electronic state K in the response functions to be derived. Denoting the energy difference between the (K,k_K)-state and the $(0,0_0)$ state by ω_{k_K} and the pure electronic energy difference as ω_K, we obtain for the linear response function (see Refs. 3 and 25)

$$\begin{aligned}\langle\langle X,Y\rangle\rangle_{\omega_y} &= P^{XY}\left\{\sum_{K,k_K\neq 0,0_0}\frac{\langle 0_0|\langle 0|X|K\rangle|k_K\rangle\langle k_K|\langle K|Y|0\rangle|0_0\rangle}{\omega_y-\omega_{k_K}}\right\}\\ &\simeq P^{XY}\left\{\sum_{k_0\neq 0_0}\frac{\langle 0_0|\langle 0|X|0\rangle|k_0\rangle\langle k_0|\langle 0|Y|0\rangle|0_0\rangle}{\omega_y-\omega_{k_0}}\right.\\ &\quad\left.+\langle 0_0|\sum_{K\neq 0}\frac{\langle 0|X|K\rangle\langle K|Y|0\rangle}{\omega_y-\omega_K}|0_0\rangle\right\}\\ &= \langle\langle\langle X\rangle^e,\langle Y\rangle^e\rangle\rangle^v_{\omega_y}+\langle\langle\langle X,Y\rangle\rangle^e_{\omega_y}\rangle^v, \end{aligned}\tag{7}$$

where we have introduced the short-hand notations

$$\langle X\rangle^e = \langle 0|X|0\rangle,\tag{8}$$

$$\langle\langle X,Y\rangle\rangle^e_{\omega_y} = P^{XY}\sum_{K\neq 0}\frac{\langle 0|X|K\rangle\langle K|Y|0\rangle}{\omega_y-\omega_K},\tag{9}$$

$$\langle\langle\langle X,Y\rangle\rangle^e_{\omega_y}\rangle^v = \langle 0_0|\langle\langle X,Y\rangle\rangle^e_{\omega_y}|0_0\rangle,\tag{10}$$

$$\langle\langle\langle X\rangle^e,\langle Y\rangle^e\rangle\rangle^v_{\omega_y} = P^{XY}\sum_{k_0\neq 0_0}\frac{\langle 0_0|\langle X\rangle^e|k_0\rangle\langle k_0|\langle Y\rangle^e|0_0\rangle}{\omega_y-\omega_{k_0}}\tag{11}$$

for the electronic expectation value, electronic linear response function, vibrational expectation value (zero-point average), and vibrational linear response function, respectively. These short-hand notations will be used in the remaining parts of this paper. In Eqs. (7), (9), and (11) $\omega_x=-\omega_y$ and P^{XY} symmetrizes with respect to simultaneous permutations of operators and frequencies with indices x and y. A molecular property described by a linear response function thus becomes a sum of terms with factors involving vibrational averaged electronic response functions and/or vibrational response functions with the electronic properties $(\langle X\rangle^e,\langle Y\rangle^e,\langle\langle X,Y\rangle\rangle^e_{\omega_y})$ as operators in the vibrational space. This type of reduction may be carried on to higher order properties. However, for higher order response functions the separation into electronic and vibrational response functions is only this simple in the static case which will become evident shortly.

The quadratic response function can be written in a SOS formalism as

$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} = P^{XYZ}\left\{\sum_{m,n\neq 0}\frac{\langle 0|X|m\rangle\langle m|\bar{Y}|n\rangle\langle n|Z|0\rangle}{(\omega_m+\omega_x)(\omega_n-\omega_z)}\right\},\tag{12}$$

where $\omega_x=-\omega_y-\omega_z$ and $\bar{Y}$ is a fluctuation operator, $\langle m|\bar{Y}|n\rangle = \langle m|Y-\langle 0|Y|0\rangle|n\rangle$, where $\bar{Y}$ upon insertion of the Born–Oppenheimer vibronic product functions gives

$$\bar{Y} = Y-\langle 0_0|\langle 0|Y|0\rangle|0_0\rangle.\tag{13}$$

Inserting the Born–Oppenheimer vibronic product functions into Eq. (12) gives

$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} = P^{XYZ}\left\{\sum_{(J,j_J),(K,k_K)\neq 0_0}\frac{\langle 0_0|\langle 0|X|J\rangle|j_J\rangle\langle j_J|\langle J|\bar{Y}|K\rangle|k_K\rangle\langle k_K|\langle K|Z|0\rangle|0_0\rangle}{(\omega_{j_J}+\omega_x)(\omega_{k_K}-\omega_z)}\right\}.\tag{14}$$

Now we simplify Eq. (14) into three contributions. One term where both J and K refer to the electronic ground state, giving a PV quadratic response term with electronic expectation values as operators (e.g., the dipole moment components). A second term where J and K both refer to excited electronic states can be simplified using the vibrational closure approximation (see below) to give a vibrationally averaged pure electronic quadratic response function. Finally, one contribution includes a pair of "mixed" summations where only one of J or K refers to the ground electronic state. Thus Eq. (14) becomes

$$\begin{aligned}\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} &\simeq P^{XYZ}\left\{\sum_{j_0,k_0\neq 0_0}\frac{\langle 0_0|\langle 0|X|0\rangle|j_0\rangle\langle j_0|\bar{Y}^v|k_0\rangle\langle k_0|\langle 0|Z|0\rangle|0_0\rangle}{(\omega_{j_0}+\omega_x)(\omega_{k_0}-\omega_z)}+\langle 0_0|\sum_{J,K\neq 0}\frac{\langle 0|X|J\rangle\langle J|\bar{Y}^e|K\rangle\langle K|Z|0\rangle}{(\omega_J+\omega_x)(\omega_K-\omega_z)}|0_0\rangle\right.\\ &\quad\left.+\sum_{j_0\neq 0_0,K\neq 0}\frac{\langle 0_0|\langle 0|X|0\rangle|j_0\rangle\langle j_0|\langle 0|Y|K\rangle\langle K|Z|0\rangle|0_0\rangle}{(\omega_{j_0}+\omega_x)(\omega_K-\omega_z)}+\sum_{k_0\neq 0_0,J\neq 0}\frac{\langle 0_0|\langle 0|X|J\rangle\langle J|Y|0\rangle|k_0\rangle\langle k_0|\langle 0|Z|0\rangle|0_0\rangle}{(\omega_J+\omega_x)(\omega_{k_0}-\omega_z)}\right\}.\end{aligned}\tag{15}$$

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In this approximation we have used closure over vibrational states, where it has been assumed that $\omega_{k_K} \simeq \omega_K$ for $K \neq 0$.

In Eq. (15) we have defined

$$\bar{Y}^v = \langle Y \rangle^e - \langle 0_0 | \langle Y \rangle^e | 0_0 \rangle, \tag{16}$$

$$\bar{Y}^e = Y - \langle 0|Y|0\rangle. \tag{17}$$

Taking the static limit ($\omega_y, \omega_z \to 0$) of Eq. (15) it can be shown that the quadratic response function can be written as

$$\langle\langle X,Y,Z\rangle\rangle_{0,0} = \langle\langle\langle X\rangle^e,\langle Y\rangle^e,\langle Z\rangle^e\rangle\rangle^v_{0,0} + \langle\langle\langle X,Y,Z\rangle\rangle^e_{0,0}\rangle^v + \tfrac{1}{2}P^{XYZ}\langle\langle\langle\langle X,Y\rangle\rangle^e_0,\langle Z\rangle^e\rangle\rangle^v_0, \tag{18}$$

where we have introduced (with general frequencies)

$$\langle\langle\langle X\rangle^e,\langle Y\rangle^e,\langle Z\rangle^e\rangle\rangle^v_{\omega_y,\omega_z} = P^{XYZ}\sum_{j_0,k_0\neq 0_0}\frac{\langle 0_0|\langle X\rangle^e|j_0\rangle\langle j_0|\bar{Y}^v|k_0\rangle\langle k_0|\langle Z\rangle^e|0_0\rangle}{(\omega_{j_0}+\omega_x)(\omega_{k_0}-\omega_z)}, \tag{19}$$

$$\langle\langle\langle X,Y,Z\rangle\rangle^e_{\omega_y,\omega_z}\rangle^v = \langle 0_0|P^{XYZ}\sum_{J,K\neq 0}\frac{\langle 0|X|J\rangle\langle J|\bar{Y}^e|K\rangle\langle K|Z|0\rangle}{(\omega_J+\omega_x)(\omega_K-\omega_z)}|0_0\rangle, \tag{20}$$

$$\langle\langle\langle\langle X,Y\rangle\rangle^e_{\omega_y},\langle Z\rangle^e\rangle\rangle^v_{\omega_z} = P^{\langle\langle X,Y\rangle\rangle^e_{\omega_y},\langle Z\rangle^e}\sum_{k_0\neq 0_0}\frac{\langle 0_0|\langle\langle X,Y\rangle\rangle^e_{\omega_y}|k_0\rangle\langle k_0|\langle Z\rangle^e|0_0\rangle}{\omega_{k_0}-\omega_z}. \tag{21}$$

Equation (18) will be easily obtained as a special case from the subsequent general considerations. In Eq. (18), we have a PV quadratic response function (i.e., a vibrational hyperpolarizability in the ground electronic state), a pure electronic quadratic response function (vibrationally averaged), and a mixed term, which is a vibrational response function with an electronic expectation value and an electronic linear response function as the operators in the vibrational space. The static equations have been derived and used before in the special case of the first hyperpolarizability, i.e., where X, Y, etc. correspond to components of the dipole moment. In this context, Bishop and Kirtman[3] denote the first and third terms in Eq. (18) as the PV contributions to the first hyperpolarizability. Occasionally the vibrational averaged term (second term) is further split up into a purely electronic contribution evaluated at the equilibrium geometry and a zero-point vibrational correction.

When the external frequencies are different from zero, the quadratic response function does not, however, come out quite this simple due to the mixed terms in Eq. (15). We note that these mixed terms are presented in Ref. 11 although not treated further. Below we reformulate and derive computationally tractable forms of the two terms. Consider the last two terms of the sum in Eq. (15),

$$\langle\langle X,Y,Z\rangle\rangle^{\mathrm{mix}}_{\omega_y,\omega_z} = P^{XYZ}\{\langle 0_0|\langle X\rangle^e K^v(-\omega_x)\langle 0|YK^e(\omega_z)Z|0\rangle|0_0\rangle + \langle 0_0|\langle 0|XK^e(-\omega_x)Y|0\rangle K^v(\omega_z)\langle Z\rangle^e|0_0\rangle\}. \tag{22}$$

In Eq. (22) we have introduced

$$K^v(\omega) = \sum_{k_0\neq 0_0}\frac{|k_0\rangle\langle k_0|}{\omega-\omega_{k_0}} \tag{23}$$

and

$$K^e(\omega) = \sum_{K\neq 0}\frac{|K\rangle\langle K|}{\omega-\omega_K}. \tag{24}$$

Introducing an asymmetric linear response function

$$\langle\langle X,Y\rangle\rangle^-_\omega = \sum_{K\neq 0}\left\{\frac{\langle 0|X|K\rangle\langle K|Y|0\rangle}{\omega-\omega_K} - \frac{\langle 0|Y|K\rangle\langle K|X|0\rangle}{-\omega-\omega_K}\right\} = \langle 0|XK(\omega)Y|0\rangle - \langle 0|YK(-\omega)X|0\rangle \tag{25}$$

and using the following identities and relations (in general notation),

$$\langle 0|XK(\omega)Y|0\rangle = \tfrac{1}{2}(\langle\langle X,Y\rangle\rangle_\omega + \langle\langle X,Y\rangle\rangle^-_\omega), \tag{26}$$

$$\langle 0|XK(-\omega)Y|0\rangle = \tfrac{1}{2}(\langle\langle Y,X\rangle\rangle_\omega - \langle\langle Y,X\rangle\rangle^-_\omega), \tag{27}$$

$$\langle\langle X,Y\rangle\rangle_\omega = \langle\langle Y,X\rangle\rangle_{-\omega}, \tag{28}$$

$$\langle\langle X,Y\rangle\rangle^-_\omega = -\langle\langle Y,X\rangle\rangle^-_{-\omega}, \tag{29}$$

Eq. (22) can be written as

$$\langle\langle X,Y,Z\rangle\rangle^{\mathrm{mix}}_{\omega_y,\omega_z} = \tfrac{1}{2}P^{XYZ}(\langle\langle\langle X\rangle^e,\langle\langle Y,Z\rangle\rangle^e_{\omega_z}\rangle\rangle^v_{\omega_y+\omega_z} + \langle\langle\langle X\rangle^e,\langle\langle Y,Z\rangle\rangle^{e-}_{\omega_z}\rangle\rangle^{v-}_{\omega_y+\omega_z}). \tag{30}$$

The second term in Eq. (30) has, to the authors' knowledge, not been considered previously and in the following we shall present different strategies for calculating and approximating it.

In the general frequency-dependent case the total quadratic response function thus becomes

$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} = \langle\langle\langle X\rangle^e,\langle Y\rangle^e,\langle Z\rangle^e\rangle\rangle^v_{\omega_y,\omega_z} + \langle\langle\langle X,Y,Z\rangle\rangle^e_{\omega_y,\omega_z}\rangle^v + \tfrac{1}{2}P^{XYZ}(\langle\langle\langle X\rangle^e,\langle\langle Y,Z\rangle\rangle^e_{\omega_z}\rangle\rangle^v_{\omega_y+\omega_z} + \langle\langle\langle X\rangle^e,\langle\langle Y,Z\rangle\rangle^{e-}_{\omega_z}\rangle\rangle^{v-}_{\omega_y+\omega_z}). \tag{31}$$

Returning to the static limit, i.e., $\omega_x=\omega_y=\omega_z=0$, it is trivially seen from Eq. (31) that one obtains the usual result, Eq. (18), as any asymmetric linear response function is zero in this limit.

The electronic problem of finding the expectation values, linear, and quadratic response functions has been solved for many electronic structure methods, e.g., Hartree–Fock,[30] DFT,[20–22] coupled cluster,[23] multiconfigurational self-consistent field,[17] and are available for use in several public available quantum chemistry program packages. The vibrational problem, however, has primarily been studied within the formalism devised by Bishop and Kirtman.[3,4,31] Vibra-

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tional expectation values have been formulated previously for vibrational self-consistent field (VSCF) and VCI wave functions,[28] and recently the calculation of linear response functions has been put forward.[25] In the following we will describe the extension to the VCI quadratic response function.

Within the VCI approach, the vibrational asymmetric linear response function is easy to find as the excitation and deexcitation spaces are solved separately (see Sec. II D) and it is thus merely a matter of subtracting the two contributions rather than adding them. For other vibrational wave function methods it is not quite as simple. A further problem lies in the electronic asymmetric linear response function, which for many methods is not well defined. Below we will detail how one may calculate or approximate the asymmetric linear response function.

C. Calculating the electronic asymmetric linear response function

By inspection of the linear asymmetric response function, Eq. (25), it is evident that this is zero in the case of a static perturbation, i.e., $\omega=0$, but for nonstatic electromagnetic fields the problem of calculating the electronic asymmetric linear response functions persists. Assuming that X, Y, and the unperturbed states are real, the linear (a)symmetric response function may be written in the alternative forms

$$\langle\langle X,Y\rangle\rangle_{\omega}^{e}=\sum_{K\neq 0}\langle 0|X|K\rangle\langle K|Y|0\rangle\frac{2\omega_K}{\omega^2-\omega_K^2}, \tag{32}$$

$$\langle\langle X,Y\rangle\rangle_{\omega}^{e-}=\sum_{K\neq 0}\langle 0|X|K\rangle\langle K|Y|0\rangle\frac{2\omega}{\omega^2-\omega_K^2}. \tag{33}$$

Equations (32) and (33) suggest the following simple approximate relation between the symmetric and asymmetric linear response functions,

$$\langle\langle X,Y\rangle\rangle_{\omega}^{e-}\simeq\frac{\omega}{\omega_K}\langle\langle X,Y\rangle\rangle_{\omega}^{e}, \tag{34}$$

for $\omega\ll\omega_K$ and assuming well-separated electronic energy levels, i.e., only one term in Eqs. (32) and (33) dominates. In Eq. (34) ω_K is the excitation energy from the electronic ground state to the lowest electronic excited state, which has a nonvanishing $\langle 0|X|K\rangle\langle K|Y|0\rangle$ residue. In this way the electronic asymmetric linear response function is approximated by the symmetric one multiplied by a factor going to zero as ω goes to zero and thus captures the static limit of the asymmetric response function. It is worth noting that the symmetric and asymmetric linear response functions have the same pole structure, i.e., both go to infinity when the external frequency matches an excitation energy, which is easily verified by Eq. (25) and the corresponding symmetric response function. The approximation suggested in Eq. (34) thus captures this feature as well.

In cases where one can get a sufficiently converged eigenspectrum with appropriate transition properties, or a similar effective spectrum, one can by SOS approaches determine the asymmetric linear response. In subsequent parts of this paper we will investigate the use of Eq. (34) compared with such more stringent (but computationally more expensive) methods for obtaining the electronic asymmetric linear response functions.

As pointed out above, a rigorous and efficient implementation of the frequency-dependent asymmetric linear response function is not for all wave function models possible because it is not a proper derivative of a (time-averaged) quasienergy. An approach, which avoids this problem and provides sufficiently accurate results to benchmark the estimate suggested in Eq. (34), exploits that the linear response functions $\langle\langle X,X\rangle\rangle_{\omega}$ for two identical perturbations can be written as a series of Stieltjes in $-\omega^2$,

$$\langle\langle X,X\rangle\rangle_{\omega}^{e}=\sum_{k=0}^{\infty}\omega^{2k}S_X(-2k-2)\quad\text{with}\quad S_X(k)=\sum_{J\neq 0}\omega_J^k f_{J,X}, \tag{35}$$

where $f_{J,X}=2\omega_J|\langle 0|X|J\rangle|^2$ is the oscillator strength for an excitation from the ground state to the Jth excited state. The Cauchy moments $S_X(-2k-2)$ with $k\geq 0$ can be implemented and evaluated efficiently as quasienergy derivatives using similar techniques as for the linear response function for any method, which allows an efficient implementation of the latter, see, e.g., Refs. 32 and 33. Series of Stieltjes have the convenient property that they can be well approximated by Padé approximants. As described, e.g., in Ref. 34, one can calculate from the moments $S_X(-2k-2)$ with $k=0,\ldots,2n-1$ the $[n,n-1]$ Padé approximant

$$[n,n-1]=\frac{P_{n-1}(\omega^2)}{Q_n(\omega^2)}, \tag{36}$$

where P_{n-1} and Q_n are (real) polynomials of, respectively, order $n-1$ and n with coefficients determined by the condition that the Taylor series of the $[n,n-1]$ approximant agrees up to $\mathcal{O}(\omega^{4n-2})$ with the series expansion in Eq. (35). By partial fraction decomposition the $[n,n-1]$ approximant can be expressed as an effective spectrum with n effective oscillatory strengths and transition energies,

$$\langle\langle X,X\rangle\rangle_{\omega}^{e}\simeq\frac{P_{n-1}(\omega^2)}{Q_n(\omega^2)}=\sum_{J=1}^{n}\frac{f_{J,X}^{(\mathrm{eff})}}{(\omega_J^{(\mathrm{eff})})^2-\omega^2}, \tag{37}$$

which converges with increasing n to the lowest transition energies within the wave function model used to calculate the linear response function or Cauchy moments. The effective spectra provide not only a compact (approximate) representation of frequency-dependent symmetric response functions, but also of the asymmetric counterparts which can be evaluated as

$$\langle\langle X,X\rangle\rangle_{\omega}^{e-}\simeq\sum_{J=1}^{n}\frac{\omega}{\omega_J^{(\mathrm{eff})}}\frac{f_{J,X}^{(\mathrm{eff})}}{(\omega_J^{(\mathrm{eff})})^2-\omega^2}. \tag{38}$$

The above procedure can also be applied to calculate asymmetric linear response functions $\langle\langle X,Y\rangle\rangle_{\omega}^{e-}$ for two different operators X and Y which fulfill Eq. (33) by expressing them as

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$$\langle\langle X,Y\rangle\rangle_{\omega}^{e-}=\tfrac{1}{2}(\langle\langle X+Y,X+Y\rangle\rangle_{\omega}^{e-}-\langle\langle X,X\rangle\rangle_{\omega}^{e-}-\langle\langle Y,Y\rangle\rangle_{\omega}^{e-}). \tag{39}$$

The Padé approximants are known to provide fast converged approximations to the frequency-dependent symmetric linear response functions if the frequency ω is below the highest transition frequencies adequately represented in the effective spectrum. Since the factor $\omega/\omega_J^{(\mathrm{eff})}$ damps the contribution from higher transitions, the errors for asymmetric response functions should be even smaller than for the symmetric ones.

D. Response functions for VCI wave functions

In the VCI framework the M-mode vibrational wave function, i.e., the vibrational wave function for a system with M vibrational degrees of freedom, is built as a sum of vibrational configurations starting from a reference configuration, usually an optimized VSCF state, and making excitations out of this,

$$|\mathrm{VCI}\rangle=|\Phi_0\rangle+\sum_{\mu}C_{\mu}\tau_{\mu}|\Phi_0\rangle. \tag{40}$$

Here the operators τ_{μ} generate excitations out of the reference VSCF ket state $|\Phi_0\rangle$. Including all one-, two-, etc. up to n-mode excitation operators results in a VCI[n] wave function and energy. Including all possible excitations in Eq. (40) one arrives at the full VCI (FVCI) wave function. The coefficients C_{μ} are determined from the Schrödinger equation by variational criteria giving the standard configuration interaction eigenvalue equation, see Refs. 26 and 27 and references therein.

For the sake of deriving vibrational response functions for a VCI state, it proves fruitful to express the time-dependent VCI state by a single exponential parametrization

$$|\bar{0}(t)\rangle=\exp(-iF(t))|\tilde{0}(t)\rangle=\exp(-iF(t))\exp(\Lambda(t))|0\rangle, \tag{41}$$

with $|0\rangle$ denoting the reference VCI vector and $F(t)$ denoting a time-dependent phase factor. $\Lambda(t)$ is an anti-Hermitian operator generating rotations in the state space and can be written in terms of state transfer operators

$$\Lambda(t)=\sum_{k}\lambda_k(t)O_k, \tag{42}$$

where

$$O_k=\begin{cases}|k\rangle\langle 0|, & k>0,\\ |0\rangle\langle k|, & k<0\end{cases} \tag{43}$$

and

$$\lambda_k=\begin{cases}\lambda_k, & k>0,\\ -\lambda_k^{*}, & k<0.\end{cases} \tag{44}$$

Using the above parametrization of the VCI state, one may derive the molecular response to arbitrary order using the machinery of response theory, as described in Refs. 19 and 35 and references therein. In our preferred approach we determine the response functions as derivatives of a time-averaged quasienergy. This follows previous work and the general equations can be easily extracted from Ref. 19. Accordingly we report here only the results in a computational convenient form.

The linear response function becomes

$$\langle\langle X,Y\rangle\rangle_{\omega_y}^{v}=\boldsymbol{\eta}^X\boldsymbol{\lambda}^Y(\omega_y)=\sum_{\pm k}\eta_k^X\lambda_k^Y(\omega_y), \tag{45}$$

where $\pm k$ refer to summation of the excitation and deexcitation parts, respectively. In Eq. (45), $\boldsymbol{\lambda}^Y(\omega_y)$ is a vector of first-order response parameters for operator Y with corresponding frequency ω_y, and the kth element of the $\boldsymbol{\eta}^X$ vector is found as

$$[\boldsymbol{\eta}^X]_k=\langle 0|[X,O_k]|0\rangle. \tag{46}$$

In a similar manner the PV quadratic response function is obtained [noting that the so-called $\boldsymbol{G}(\omega_y,\omega_z)$ matrix is zero for a VCI state, as it contains an odd number of state transfer operators in addition to the unperturbed Hamiltonian, see Ref. 19] as

$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}^{v}=\frac{1}{2}P^{XYZ}\boldsymbol{F}^X\boldsymbol{\lambda}^Y(\omega_y)\boldsymbol{\lambda}^Z(\omega_z), \tag{47}$$

$$=\frac{1}{2}P^{XYZ}\sum_{\pm k}\sigma_k^{XY}(\omega_y)\lambda_k^Z(\omega_z). \tag{48}$$

Note that only linear response parameters are needed in agreement with the $2n+1$ rule. In Eq. (47), P^{XYZ} generates all six permutations of operators and corresponding frequencies with $\omega_x=-(\omega_y+\omega_z)$. $\sigma^{XY}(\omega_y)$ is a response vector $\lambda^Y(\omega_y)$ transformed by the so-called $\boldsymbol{F}^X$ matrix. The klth element of the $\boldsymbol{F}^X$ matrix is found as

$$[\boldsymbol{F}^X]_{kl}=\tfrac{1}{2}P(O_k,O_l)\langle 0|[[X,O_k],O_l]|0\rangle. \tag{49}$$

The matrix vector contraction is done directly so one avoids storing the $\boldsymbol{F}^X$ matrix

$$\boldsymbol{\sigma}^{XY}(\omega_y)=\boldsymbol{F}^X\boldsymbol{\lambda}^Y(\omega_y). \tag{50}$$

In VCI theory, the excitation and deexcitation spaces decouple, thus reducing the computational complexity. We note that this decoupling is what allows us to easily calculate vibrational asymmetric linear response functions, as discussed in Sec. II B. This is done simply by subtracting the deexcitation part rather than adding it, i.e.,

$$\langle\langle X,Y\rangle\rangle_{\omega_y}^{v-}=\sum_{k>0}\eta_k^X\lambda_k^Y(\omega_y)-\sum_{k<0}\eta_k^X\lambda_k^Y(\omega_y). \tag{51}$$

Constructing the quadratic response function for VCI thus requires the solution of a maximum of six first-order parameter equations corresponding to $(X,\pm\omega_x)$, $(Y,\pm\omega_y)$, and $(Z,\pm\omega_z)$. The linear response equations to be solved are

$$\sum_{l>0}\{A_{kl}-\omega_y\delta_{kl}\}\lambda_l^Y(\omega_y)=\eta_k^Y, \tag{52}$$

where also $k>0$. Here

$$A_{kl}=\langle\Psi_k|H_o|\Psi_l\rangle-\delta_{kl}\langle\Psi_o|H_o|\Psi_o\rangle. \tag{53}$$

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These response equations are solved simultaneously using standard reduced space iterative schemes.[18] The response excitation energies are determined from the position of the poles of the linear response function. These are positioned at the solutions to the generalized eigenvalue equation

$$\boldsymbol{AV} = \boldsymbol{\omega V}, \tag{54}$$

where $\boldsymbol{\omega}$ is a diagonal matrix with the excitation energies on the diagonal and $\boldsymbol{V}$ is a matrix containing the response eigenvectors as columns. The VCI response theory eigenvalues are equivalent to finding the excited states by diagonalizing the VCI Hamiltonian matrix as usual within the given VCI space, as seen from Eq. (53). The transition moments for an excitation from the vibrational ground state to the final state f are found from the residues of the linear response functions as

$$\langle f|Y|o\rangle = T^Y_{fo} = \sum_{k>0} \eta^Y_k V_{kf}. \tag{55}$$

Transition moments between two excited states are calculated from the residues of the quadratic response functions as

$$\langle f|Y|i\rangle = T^Y_{if} = \sum_{k,l>0} \boldsymbol{F}^Y_{-kl} V_{ki} V_{lf}. \tag{56}$$

Equations (55) and (56) make it possible to construct the SOS linear and quadratic response functions by evaluating the terms in Eq. (15) directly. When including the full excitation space the "exact" response function is obtained and hence this route, however, slow and tedious, provides an excellent reference for the response functions obtained via the response theory approach.

Transition moments between any states as well as the calculation of PV quadratic response functions using the VCI wave function have been implemented in the MIDASCPP (Ref. 36) program, augmenting the existing VCI linear response function implementation. The implementation also includes modules for automatically building the total linear and quadratic response functions.

E. Frequency dispersion analysis

The PV quadratic response function [i.e., first term of Eq. (15)] does not capture the correct physical behavior of an excited state in all ways as it does not include the fact that excited states have finite lifetimes for a number of reasons. This causes that the response functions become infinite when a frequency of a perturbing field matches an excitation energy. Whereas this is also a problem in electronic structure theory, where the problem has been addressed in recent years,[37] the effect may be much more pronounced in the vibrational counterpart due to the inherent low excitation frequencies in vibrational problems. This has the consequence that even for small systems an optical frequency will correspond to a place in the spectrum with a very high density of states and hence easily match an excitation frequency. It should be mentioned, however, that the vibrational oscillator strengths decrease rapidly with increasing excitation quanta and the actual contribution from these states should be small.

The effect of finite lifetimes can phenomenologically be accounted for via a complex damping factor in the form[37–40]

$$\omega_n \rightarrow \omega_n - i\gamma_n \tag{57}$$

with

$$\gamma_n = \frac{1}{\tau_n}, \tag{58}$$

with τ_n as the lifetime of the nth excited state.

At this point we note that in recent years there has been a discussion taking place as to whether the sign of the damping factors in the terms in, e.g., a linear response function should be of the same sign or opposite sign.[38–42] The two conventions are, for obvious reasons, referred to as the same-sign and opposite-sign conventions, see, e.g., Ref. 42. In this work we use the strategy provided by the work of Norman *et al.*,[37] where damping terms are introduced in the Liouville equation, which govern the time development of a (quantum mechanical) ensemble, see, e.g., Ref. 43. Using this equation in combination with perturbation theory provides damped response functions to, in principle, arbitrary order. The advantage of this approach is that the sign of γ in the individual contributions is unambiguous. As a consequence, our expressions, as advocated by Buckingham and Fischer,[39,40] obey the opposite-sign convention, and the linear response function becomes, assuming real operators and real states,

$$\langle\langle X,Y\rangle\rangle_\omega = \sum_{m\neq 0}\left\{\frac{\langle 0|X|m\rangle\langle m|Y|0\rangle}{\omega_m - i\gamma_m - \omega} + \frac{\langle 0|Y|m\rangle\langle m|X|0\rangle}{\omega_m + i\gamma_m + \omega}\right\}, \tag{59}$$

where the sign of γ_m follows the sign of the frequency of the perturbing field. Taking only the real part of Eq. (59) yields

$$\langle\langle X,Y\rangle\rangle_{\omega_y} = P^{XY}\sum_{m\neq 0}\left\{\frac{\langle 0|X|m\rangle\langle m|Y|0\rangle(\omega_y - \omega_m)}{(\omega_y - \omega_m)^2 + \gamma^2}\right\}. \tag{60}$$

Switching to the quadratic response function, one obtains[37]

$$\begin{aligned}\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} = P^{YZ}\sum_{m,n\neq 0}\Bigg\{&\frac{\langle 0|X|m\rangle\langle m|\bar{Y}|n\rangle\langle n|Z|0\rangle}{(\omega_m + \omega_x - i\gamma)(\omega_n - \omega_z - i\gamma)} \\ &+ \frac{\langle 0|Z|m\rangle\langle m|\bar{Y}|n\rangle\langle n|X|0\rangle}{(\omega_m + \omega_z + i\gamma)(\omega_n - \omega_x + i\gamma)} \\ &+ \frac{\langle 0|Y|m\rangle\langle m|\bar{X}|n\rangle\langle n|Z|0\rangle}{(\omega_m + \omega_y + i\gamma)(\omega_n - \omega_z - i\gamma)}\Bigg\}.\end{aligned} \tag{61}$$

The real part of Eq. (61) is

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$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z} = P^{YZ} \sum_{m,n\neq 0} \left\{ \frac{\langle 0|X|m\rangle\langle m|\bar{Y}|n\rangle\langle n|Z|0\rangle[(\omega_m+\omega_x)(\omega_n-\omega_z)-\gamma^2]}{[(\omega_m+\omega_x)^2+\gamma^2][(\omega_n-\omega_z)^2+\gamma^2]} \right.$$
$$\left. + \frac{\langle 0|Z|m\rangle\langle m|\bar{Y}|n\rangle\langle n|X|0\rangle[(\omega_m+\omega_z)(\omega_n-\omega_x)-\gamma^2]}{[(\omega_m+\omega_z)^2+\gamma^2][(\omega_n-\omega_x)^2+\gamma^2]} + \frac{\langle 0|Y|m\rangle\langle m|\bar{X}|n\rangle\langle n|Z|0\rangle[(\omega_m+\omega_y)(\omega_n-\omega_z)+\gamma^2]}{[(\omega_m+\omega_y)^2+\gamma^2][(\omega_n-\omega_z)^2+\gamma^2]} \right\}. \tag{62}$$

For the quadratic response function some of the permutational symmetry is lost compared with the nondamped quadratic response function. In the off-resonance regions, i.e., where γ can be safely neglected, the ordinary quadratic response function is retained.

In Eqs. (60)–(62) all lifetimes γ_n have been set equal to a common γ for simplicity and because they are, at best, difficult to estimate. When the damping factors are not zero, the response functions become finite even when an excitation energy matches one of the optical frequencies.

The inclusion of damping via the SOS approach described by Eq. (62) has been implemented in the MIDASCPP program. The problem is that this SOS way of calculating the molecular response is intractable for larger systems but can be illustrative for analysis purposes as it provides access to a response function at all frequencies. A pragmatic approach to include at least some of the attractive aspects of both strategies, i.e., response theory and damping SOS, is to approximate the linear and quadratic response functions by

$$\langle\langle X,Y\rangle\rangle_{\omega}^{v} \simeq \langle\langle X,Y\rangle\rangle_{\omega=0}^{v} f_{\omega}^{XY}, \tag{63}$$

$$\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}^{v} \simeq \langle\langle X,Y,Z\rangle\rangle_{\omega_y=0,\omega_z=0}^{v} f_{\omega_y,\omega_z}^{XYZ}, \tag{64}$$

where f_{ω}^{XY} and $f_{\omega_y,\omega_z}^{XYZ}$ are given by

$$f_{\omega}^{XY} = \frac{\langle\langle X,Y\rangle\rangle_{\omega}^{\mathrm{SOS}}}{\langle\langle X,Y\rangle\rangle_{\omega=0}^{\mathrm{SOS}}}, \tag{65}$$

$$f_{\omega_y,\omega_z}^{XYZ} = \frac{\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}^{\mathrm{SOS}}}{\langle\langle X,Y,Z\rangle\rangle_{\omega_y=0,\omega_z=0}^{\mathrm{SOS}}}, \tag{66}$$

where $\langle\langle X,Y\rangle\rangle_{\omega}^{\mathrm{SOS}}$ and $\langle\langle X,Y,Z\rangle\rangle_{\omega_y,\omega_z}^{\mathrm{SOS}}$ are linear and quadratic vibrational response functions, respectively, calculated via the SOS approach. It should be noted that the use of these functions provides the exact result in the case of a static frequency and when including all states in the SOS response functions. For actual applications, the SOS expressions are in either case limited to a few states. Via this approximation, one may use Eqs. (60) and (61) to include the effect of finite lifetimes of the excited vibrational states.

In the calculation of linear and quadratic response functions the undamped response theory approach will potentially provide unphysical results for some frequencies due to the neglect of damping and/or the response equations will be difficult to converge, which can be a severe problem in practice for large perturbing frequencies, where the density of vibrational states may be large. The use of the dispersion functions f_{ω}^{XY} and $f_{\omega_y,\omega_z}^{XYZ}$ of Eqs. (65) and (66) provides a strategy for circumventing these problems. The pure SOS route, on the other hand, will be difficult or even impossible to realize due to the large number of states needed for convergence of the SOS. The use of Eqs. (65) and (66) is thus pragmatic, but does attempt to get the best of both approaches.

In Sec. IV we will benchmark this approximate method for obtaining frequency-dependent (hyper)polarizabilities with and without damping included.

III. COMPUTATIONAL DETAILS

The method described in Sec. II for calculating PV contributions to the quadratic response functions has been applied to water, formaldehyde, hydrogen fluoride, and pyrrole. The molecules are oriented according to their molecular dipole moments with the direction of the dipole moment of the equilibrium geometries coinciding with the Cartesian z-axis. The nonlinear molecules are in the yz-plane. From this point we specialize our treatment of the quadratic response functions to the special case of the SHG part of the first hyperpolarizability, although we stress that other more general properties may be handled without any modification of the code in MIDASCPP.[36] The isotropic frequency-dependent first hyperpolarizability is given by

$$\beta_{\parallel} = \frac{1}{5} \sum_{i=x,y,z} (\beta_{zii} + \beta_{izi} + \beta_{iiz}). \tag{67}$$

For water and formaldehyde the PESs and dipole moment surfaces are based on CCSD(T) (Ref. 44) in the aug-cc-pVTZ basis by Dunning and co-workers,[45–47] while the polarizability surfaces are calculated by CCSD/aug-cc-pVTZ, as reported in Refs. 25 and 28. The hyperpolarizabilities required for calculating the zero-point vibrational averages are calculated at the same level of theory. All surfaces related with water and formaldehyde are fourth order Taylor expansions around the equilibrium geometry and the notation used to specify the surfaces has been adapted from Ref. 25, i.e., V4M4T/P2M4T means that the PES is a fourth order Taylor expansion coupling up to four modes and the property surface is also a fourth order Taylor expansion but including only up to two mode couplings.

For the FH molecule the CC3/d-aug-cc-pVQZ level of theory is used for all properties. In this case the molecular properties have been calculated for a set of displaced geometries to which a number of additional points have been added by cubic spline interpolation. To this set of points a

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TABLE I. Individual parts of the PV quadratic response function (SHG) calculated for the water molecule as a function of the VCI mode excitation level at different optical frequencies and at the static limit using V3M4T/P3M4T potential and property surfaces, respectively.

	$\omega=0.000$		$\omega=0.0428$		$\omega=0.0656$	
Mode excitation level	β_{ZZZ}	β_{ZYY}	β_{ZZZ}	β_{ZYY}	β_{ZZZ}	β_{ZYY}
1	−4.682	−0.2352	-1.670×10^{-3}	−0.012 65	-2.817×10^{-4}	-4.596×10^{-3}
2	−5.126	−0.4615	-2.150×10^{-3}	-8.311×10^{-4}	-3.487×10^{-4}	-1.600×10^{-4}
3	−5.267	−0.4739	-1.963×10^{-3}	-5.510×10^{-4}	-3.343×10^{-4}	-9.312×10^{-5}

high degree polynomial has been fitted using singular value decomposition. The procedure follows closely the one described in Ref. 48.

The asymmetric linear dipole-dipole response functions for FH have been calculated by the procedure described in Sec. II C, from effective spectra with three terms obtained from the [3,2] Padé approximants, which were calculated from the Cauchy moments $S(-2k-2)$ with $k=0,\ldots,5$. The Cauchy moments and response functions were computed at CC3/d-aug-cc-pVQZ level of theory using the implementation in the DALTON program described in Ref. 33. The Cauchy moments and response functions were computed for a total set of 40 bond distances between 1.15 and 5.0 bohr.

For pyrrole the PES has been calculated using the grid approach, as described in Ref. 29, the reader is referred to this work for details. The grid is based on a $32_1 16_{3/4}$ set of coarse grid points and thus defines a potential coupling at most two modes. The molecular property surfaces have been obtained from either 32_1 or $32_1 8_{1/2}$ sets of coarse grid points. The electronic structure calculations have been carried out at the DFT level employing the CAM-B3LYP hybrid exchange correlation functional[49] and the pol basis set by Sadlej.[50] The quadratic response implementation of Sałek *et al.*[22] was used.

The DALTON electronic structure program[51] has been used for all electronic structure calculations. The vibrational structure calculations have been performed using VCI linear[25] and quadratic response function methods. Harmonic oscillator (HO) one-mode basis sets were used where the HO exponents in each case were chosen in accordance with the harmonic part of the potential. The size of the basis is characterized by the HO quantum number. From the primitive HO basis an optimized set of models is obtained in a VSCF optimization and subsequently used in the VCI calculations. If not stated otherwise seven HO basis functions ($v=0,\ldots,6$) are used, and all VSCF modals are used in the VCI calculations. Vibrational basis sets of this size have been found previously to provide results converged with respect to the one-mode basis.[25] For formaldehyde, the VCI[4] calculations employed only the four lowest VSCF modals for easier convergence of the equations. However, a similar calculation with a limited modal space using VCI[3] produced virtually no differences between the truncated and untruncated VSCF modal spaces.

IV. SAMPLE CALCULATIONS

A. Mode excitation level

In Secs. IV A 1 and IV A 2 we present an analysis of the PV quadratic response function [i.e., first term of Eq. (15)] of water and formaldehyde in terms of the highest included mode excitation level and the frequency dependence.

1. Water

In Table I the individual Cartesian directional components of the PV quadratic response function for the water molecule are given for the mode excitation levels used in the VCI calculation for the static limit as well as for a few optical frequencies.

It is immediately clear from Table I that at optical frequencies the vibrational contribution to the first hyperpolarizability becomes very small. This may easily be understood from the form of the exact expression of the PV quadratic response function, Eq. (15) (first term). Optical frequencies are much larger than the vibrational excitation energies and hence the denominator will cause the absolute size of the PV contribution to the hyperpolarizabilities of a small molecule like water to become small, unless the optical frequency matches a vibrational excitation frequency.

The results illustrate that in order to obtain converged results for this three-mode system, FVCI calculations need to be performed.

2. Formaldehyde

In Table II the individual Cartesian directional components of the PV quadratic response function for formaldehyde are given for the mode excitation level used in the VCI calculation for two optical frequencies as well as for the static case. Similar to what was observed for the water molecule, the hyperpolarizability components at optical frequencies are very small.

The results in Table II clearly illustrate that VCI[1] is insufficient for calculating PV contributions to quadratic response functions, providing results that in some cases even have the wrong sign. Switching to VCI[2] provides a better description of the contributions for all frequencies and does at least correct the signs of the individual contributions. Including in the description of the vibrational wave function, also Hartree products, which are excited in three modes simultaneously, provide results which in all cases are very close to the FVCI limit (corresponding to VCI[6]) in abso-

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TABLE II. Individual parts of the PV quadratic response function calculated for formaldehyde as a function of the VCI mode excitation level at different optical frequencies and at the static limit using V4M4T/P4M4T potential and property surfaces, respectively.

	VCI[1]	VCI[2]	VCI[3]	VCI[4]	VCI[5]	VCI[6]
Static						
β_{ZZZ}	3.504	3.649	3.812	3.808	3.808	3.808
β_{ZXX}	0.2437	−0.1413	−0.1397	−0.1422	−0.1426	−0.1426
β_{ZYY}	1.948	4.034	4.236	4.240	4.241	4.241
β_{XXZ}	0.2437	−0.1413	−0.1397	−0.1422	−0.1426	−0.1426
β_{YYZ}	1.948	4.034	4.236	4.240	4.241	4.241
ω=0.0428						
β_{ZZZ}	5.742×10^{-3}	9.402×10^{-3}	9.350×10^{-3}	9.351×10^{-3}	9.351×10^{-3}	9.351×10^{-3}
β_{ZXX}	-4.034×10^{-3}	7.954×10^{-5}	6.481×10^{-5}	7.094×10^{-5}	7.303×10^{-5}	7.314×10^{-5}
β_{ZYY}	4.089×10^{-2}	1.067×10^{-2}	9.698×10^{-3}	9.623×10^{-3}	9.636×10^{-3}	9.636×10^{-3}
β_{XXZ}	2.061×10^{-3}	-2.298×10^{-4}	-2.114×10^{-4}	-2.146×10^{-4}	-2.157×10^{-4}	-2.157×10^{-4}
β_{YYZ}	-1.565×10^{-2}	8.952×10^{-3}	9.869×10^{-3}	9.914×10^{-3}	9.909×10^{-3}	9.909×10^{-3}
ω=0.0656						
β_{ZZZ}	9.827×10^{-4}	1.531×10^{-3}	1.573×10^{-3}	1.573×10^{-3}	1.573×10^{-3}	1.573×10^{-3}
β_{ZXX}	-1.721×10^{-3}	1.530×10^{-5}	6.812×10^{-6}	9.829×10^{-6}	1.074×10^{-5}	1.079×10^{-5}
β_{ZYY}	1.530×10^{-2}	2.028×10^{-3}	1.646×10^{-3}	1.616×10^{-3}	1.620×10^{-3}	1.620×10^{-3}
β_{XXZ}	8.681×10^{-4}	-4.644×10^{-5}	-3.503×10^{-5}	-3.656×10^{-5}	-3.700×10^{-5}	-3.703×10^{-5}
β_{YYZ}	-6.849×10^{-3}	1.351×10^{-3}	1.618×10^{-3}	1.635×10^{-3}	1.633×10^{-3}	1.633×10^{-3}

lute terms. The β_{ZXX} component at ω=0.0428 a.u. and ω=0.0656 a.u. is more difficult in relative terms, but is quite small and hence of minor importance.

B. Sum-over-states results

The SOS results presented in this section are based on excitation eigenenergies and associated eigenstates calculated via response theory and ordered according to increasing energy. The contributions are added to the SOS results in the same manner, i.e., a SOS response function with three states includes the three lowest excited vibrational states, which are not necessarily the first three fundamentals.

1. Convergence with respect to the number of vibrational states

In Fig. 1 the convergence of the SOS PV quadratic response function of water is presented. It is seen that the convergence is very fast with respect to the number of states included, the PV quadratic response function being converged to within 10^{-5} a.u. including about 30 states of the 342 possible states at the VCI[3]/v=6 level. This finding is in line with what has been observed for the PV linear SOS response function.[25] It is expected that for a rigid few-mode system the response function should converge quite fast with the number of states included in the SOS approach, as the magnitude of individual contributions depends on the transition moments, which are typically larger for example for fundamentals compared with higher overtones for such systems. However, the number of fundamentals and other few-mode excited states increases with the size of the system, which means that the SOS response function may require more and more states to be calculated. This in turn means that one must solve the VCI response eigenvalue equations (Eq. (54)) for more and more states, i.e., one extra eigenvalue must be found for each included state, thus increasing the computational cost significantly. In contrast, the response approach requires the same number of equations to be solved regardless of the size of the system.

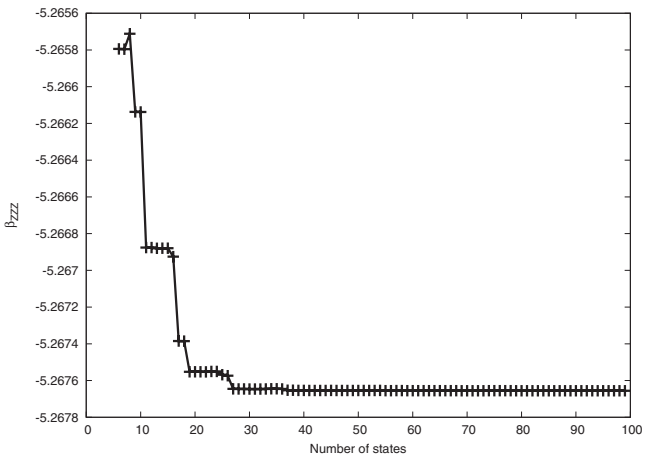


FIG. 1. Convergence of the *ZZZ* part of the PV quadratic response function for water as a function of the number of states included. Based on a VCI[3] calculation using 3M4T potential and property surfaces.

2. Frequency dispersion

Before analyzing the results for the frequency dispersion, we note that the undamped response function has poles where the frequency of the perturbing field matches an excitation frequency. In addition, the quadratic response function will have poles where two times the frequency of the perturbing field matches an excitation frequency due to the frequency sum rule $\omega_x=-\omega_y-\omega_z$ with $\omega_y=\omega_z=\omega$ for SHG. For the water molecule the first four excitation energies are 7.23×10^{-3}, 14.34×10^{-3}, 17.04×10^{-3}, and 17.41×10^{-3} a.u., corresponding to the HOH bending fundamental, the first HOH bending overtone, the symmetric OH stretching fundamental, and the asymmetric OH stretching

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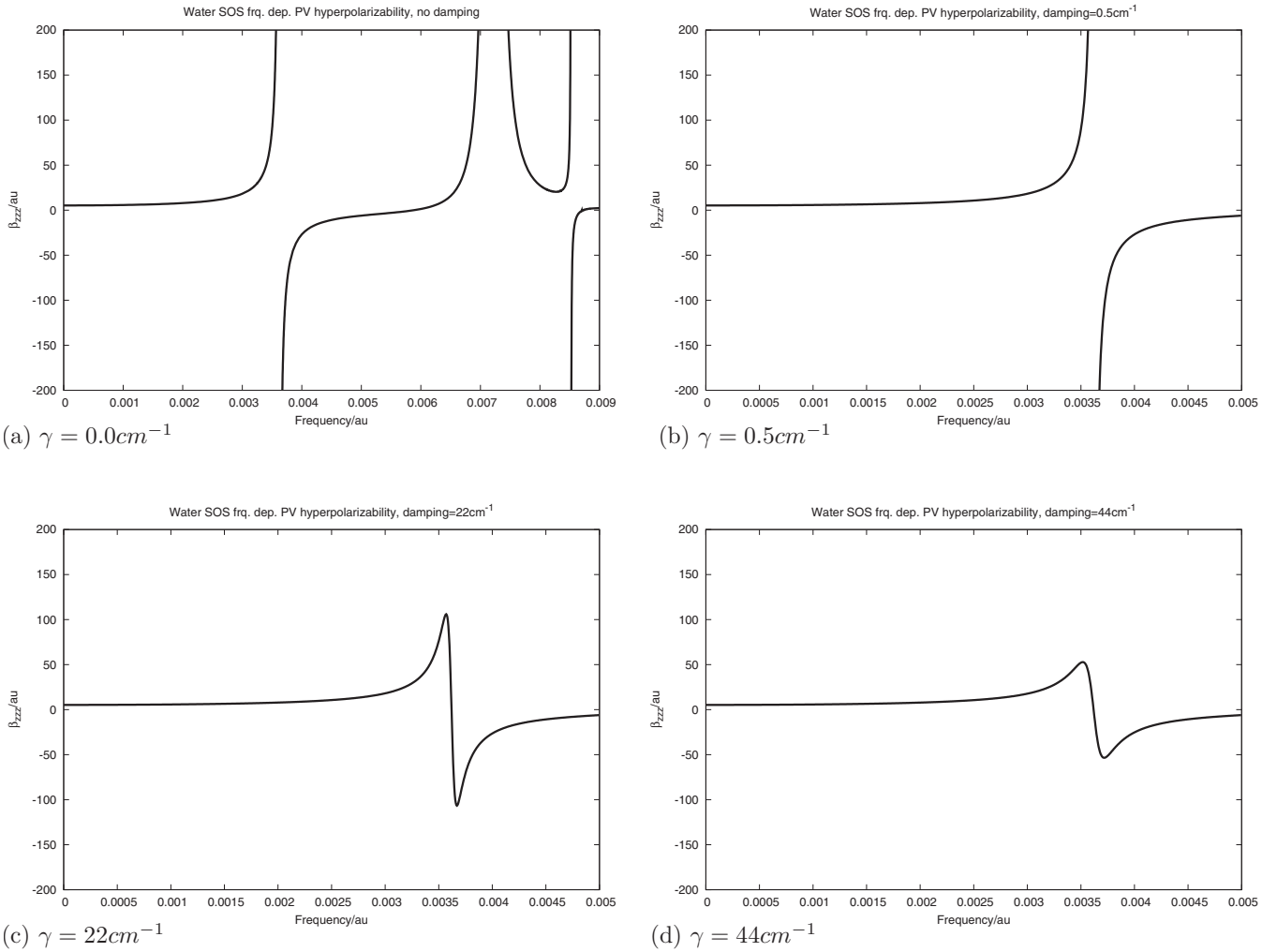


FIG. 2. SHG PV β_{zzz} for water as a function of external frequency calculated for different damping factors.

fundamental, respectively. Due to the sum rule for the quadratic response function, the half excitation frequencies are relevant as well. These are 3.62×10^{-3}, 7.17×10^{-3}, 8.52×10^{-3}, and 8.71×10^{-3} a.u.

In Fig. 2(a) the PV β_{zzz} for water is shown as a function of the frequency of the perturbing field where no damping factor has been included. From this figure it is evident that the first pole occurs at a frequency of 3.62×10^{-3} a.u.. The second pole is observed at 7.17×10^{-3} a.u. (first HOH bending overtone), but the structure of this pole is markedly different from the first one. This is due to a near coalescence of this pole with the HOH bending fundamental observed at 7.23×10^{-3} a.u.. The pole at 7.17×10^{-3} a.u. goes to positive infinity from the low frequency side, while it goes to negative infinity from the high frequency side. The opposite is true for the pole at 7.23×10^{-3}, thus providing a seemingly strange pole profile going to positive infinity from either side. The part in between is outside the y-range of the figure. The last pole observed corresponds to the asymmetric OH stretching mode and is rather sharp. The pole corresponding to the asymmetric stretching mode is not observed for β_{zzz} for symmetry reasons.

In Figs. 2(b)–2(d) we have focused on the first pole and included damping factors of 0.5, 22, and 44 cm^{-1}, respectively. For γ=0.5 cm^{-1} the poles are still sharp and localized, whereas for γ=22 cm^{-1} and γ=44 cm^{-1} the pole becomes significantly damped as the denominator in Eq. (61) never drops below γ^2.

C. Frequency dispersion function

We now discuss the results obtained by approximating the frequency-dependent response function by a static response function calculated by response theory multiplied by a frequency dispersion function, as in Eqs. (65) and (66). In Fig. 3 we present the convergence of the error of the PV $\beta_{ZZZ}(\omega,\omega)$ component for water with respect to the number of states included in the dispersion function, i.e., the values plotted are

$$\langle\langle Z,Z,Z\rangle\rangle_{\omega_y=0,\omega_z=0} f^{ZZZ}_{\omega_y,\omega_z} - \langle\langle Z,Z,Z\rangle\rangle^{\mathrm{SOS}}_{\omega_y,\omega_z}. \tag{68}$$

Figures 3(a) and 3(b) are without and with a damping factor of 22 cm^{-1}, respectively. Figure 3(a) illustrates that the convergence of the estimated frequency-dependent $\beta_{ZZZ}(\omega,\omega)$ component is very fast with respect to the number of states included in the dispersion function when ne-

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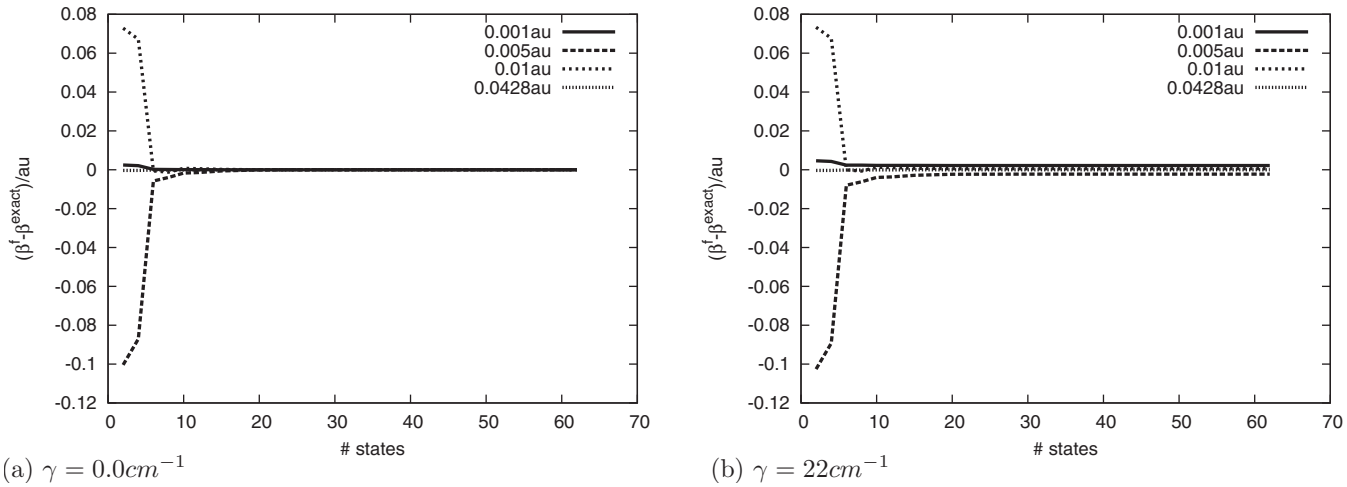


FIG. 3. SHG PV β_{zzz} difference between exact SOS expression and the dispersion function estimated equivalent for water. See text for details.

glecting the effect of finite lifetimes. Including the effect of finite lifetimes does not change this conclusion, as is evident from the plot in Fig. 3(b).

The dispersion function thus seems to be a reasonable approximation for these molecules, as well as a pragmatic way for investigating the effect of finite lifetimes.

D. Total response

In Sec. IV B we discussed and tested the new implementation of the PV quadratic response function. We now switch to the calculation of the total response, i.e., electronic and vibrational as given by Eq. (31) in the general case. The excitation energies used in the approximation of the electronic asymmetric linear response functions are presented in Table III. In the following we will compute the total rotationally averaged first hyperpolarizability as

$$\beta_{\|}^{\mathrm{tot}} = \beta_{\|}^{\mathrm{eq}} + \beta_{\|}^{zpvc} + \beta_{\|}^{pvq} + \beta_{\|}^{pvl+} + \beta_{\|}^{pvl-} = \beta_{\|}^{\mathrm{eq}} + \beta_{\|}^{v,\mathrm{tot}}, \tag{69}$$

where the terms correspond to the equilibrium value, the ZPVC, the PV quadratic response function, and the PV symmetric and asymmetric linear response functions, respectively.

1. Hydrogen fluoride

As stated in Sec. II one is faced with the problem of calculating the electronic asymmetric linear response function and we begin our discussion of the FH molecule with addressing this issue. For this particular one-mode system we have access to the exact electronic asymmetric linear response functions, see the discussion in Sec. II C.

In Fig. 4 we present the total vibrational contributions to the quadratic response function $\beta_{\|}$ as a function of the external frequency with the asymmetric linear response function calculated by the above sketched exact method and the approximate method set up in Sec. II, i.e., using the electronic excitation energies as in Eq. (34). Note that the static limit has not been included as this is trivially equal in the two approaches due to the asymmetric response function being zero.

The difference between the results for $\beta_{\|}$ with the asymmetric electronic linear response functions calculated by the two different approaches is rather constant for the frequencies considered in the analysis. This may be explained by the fact that the studied frequency range is rather narrow and, as evident from Table III, quite far from the lowest electronic excitation energy, which is found at 0.39 a.u. The error introduced in $\beta_{\|}$ for the frequencies studied here is in all cases about 1% for the total vibrational contribution (ZPVC and PV) and the overall error for the total $\beta_{\|}$ is less than 0.2%.

TABLE III. Excitation energies used in the approximation of electronic asymmetric linear response functions. The electronic structure models used for the individual molecules are the same as those used to construct the molecular property surfaces, see text for details. Values are in eV.

Component	FH	Water	Formaldehyde	Pyrrole
X	10.49	7.622	9.371	5.879
Y	10.49	11.20	7.237	6.142
Z	13.51	9.885	8.214	7.332

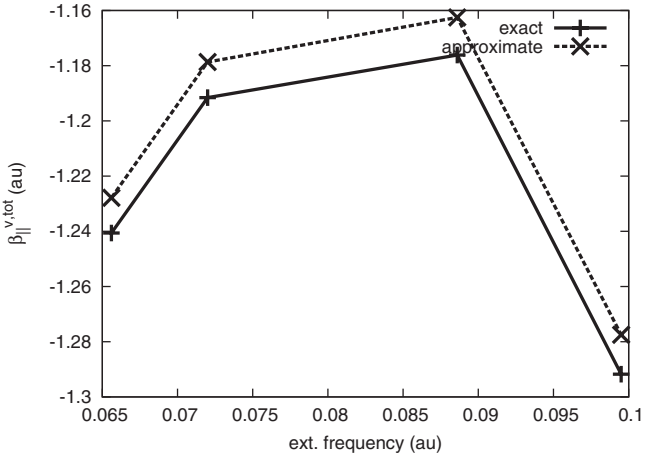


FIG. 4. The total vibrational contributions to $\beta_{\|}$ for hydrogen fluoride calculated using either the exact or approximate electronic asymmetric linear response functions (see text for details) as a function of external frequency. The full curve represents the exact values and the broken curve the approximate results.

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TABLE IV. Total vibrational contributions to $\beta_{\parallel}(\omega,\omega)$ for hydrogen fluoride calculated at external frequencies of ω=0.0, 0.0656, 0.0720, 0.0885, and 0.0995 a.u. Values are in atomic units.

	0.0	0.0656	0.0720	0.0885	0.0995
$\beta_{\parallel}^{pvl+}$	7.025	−0.4551	−0.3771	−0.2527	−0.2049
$\beta_{\parallel}^{pvl-}$	0.000	−0.1714	−0.1737	−0.1845	−0.1956
$\beta_{\parallel}^{pvq}$	−0.1887	0.0000	0.0000	0.0000	0.0000
$\beta_{\parallel}^{zpvc}$	−0.5076	−0.6142	−0.6407	−0.7389	−0.8913
$\beta_{\parallel}^{\text{vib-tot}}$	6.329	−1.241	−1.192	−1.176	−1.292
$\beta_{\parallel}^{\text{eq}}$	−7.342	−8.162	−8.350	−8.976	−9.528
$\beta_{\parallel}^{\text{tot}}$	−1.013	−9.403	−9.542	−10.15	−10.82
Expt.[a]		-10.88 ± 0.95			

[a]From Ref. 54. The frequency of the measurement is 0.0656 a.u.

This fact, together with Fig. 4, clearly shows that the approximate form gives the major part of the contribution and is a cost-efficient approach.

In Table IV we present the contributions to the rotationally averaged first hyperpolarizability for the hydrogen fluoride (FH) molecule at several optical frequencies as well as the static limit. From Table IV we note that the asymmetric linear response function is zero in the static limit but increases in magnitude with increasing frequency and becomes of similar magnitude as the symmetric linear response function at the optical frequencies. This is noteworthy as this term has so far been neglected.

In the range of optical frequencies studied here, the symmetric and asymmetric linear response functions have opposite frequency dependencies. The magnitude of the symmetric linear response function decreases in magnitude while its asymmetric analog increases in magnitude.

It is seen that the two linear response terms account for 30%–50% of the total vibrational contribution at optical frequencies. At optical frequencies the contribution from the PV quadratic response function is found to be negligible. Generally the pure electronic term, i.e., the response at the equilibrium geometry, is dominating the total $\beta_{\parallel}$. However, at all optical frequencies the collected vibrational contributions, i.e., PV and ZPVC, account for more than 10% of the total response and are therefore clearly non-negligible. In the static limit, the PV symmetric linear response function provides a very large contribution to the first hyperpolarizability.

The combined electronic and vibrational response function at a frequency of 0.0656 a.u. amounts to −9.402 a.u. This value agrees well with the one found in Ref. 52 (where $\beta_{\parallel}^{pvl-}$ was based on a SOS approach) and we believe that this value is of high accuracy. With the new results presented above, we may estimate the remaining uncertainties from different sources, i.e., from the use of incomplete basis sets, correlation effects, and vibrational effects. Based on these values we arrive at a best estimate of $\beta_{\parallel}$(0.0656 a.u.) of -9.63 ± 0.21 a.u.. This value is in contrast to the experimental value of -10.88 ± 0.95 a.u., which has, however, a rather large error bar. The results and estimated remaining effects are presented in Table V.

TABLE V. SHG first hyperpolarizability of FH at external frequency of 0.0720 a.u. Results are in atomic units.

	$\beta_{\parallel}^{\text{SHG}}$(0.0656 a.u.)
CC3/d-aug-cc-pVQZ equilibrium	−8.35
Estimated remaining basis effects	-0.10 ± 0.10 [a]
Estimated remaining corresponding effects	$+0.07 \pm 0.07$ [b]
Zero-point vibrational correction	-0.61 ± 0.01 [c]
PV contribution	-0.64 ± 0.03 [c]
Best theoretical estimate	-9.63 ± 0.21
Expt.[d]	-10.88 ± 0.95

[a]Difference between CCSD/d-aug-cc-pVQZ and CCSD/q-aug-cc-pVQZ results.
[b]Difference between CC3/d-aug-cc-pVDZ and full configuration interaction (FCI)/aug-cc-pVDZ results, Ref. 55.
[c]CC3/d-aug-cc-pVQZ result with the difference between CC3/d-aug-cc-pVTZ and CC3/d-aug-cc-pVQZ surface based vibrational calculations as uncertainty (this work).
[d]From Ref. 54.

2. Water

The total quadratic response functions obtained for the water molecule are presented in Table VI. For the optical frequencies studied here the contribution from the asymmetric linear response term [now evaluated through the approximation in Eq. (34)] is smaller than the symmetric one, but as observed for hydrogen fluoride, the difference between these two terms narrows as the external frequency increases.

TABLE VI. Total vibrational contributions to $\beta_{\parallel}(\omega,\omega)$ for water calculated at external frequencies of ω=0.0, 0.0428, and 0.0656 a.u. Values are in atomic units.

	0.0	0.0428	0.0656
$\beta_{\parallel}^{pvl+}$	6.090	−0.5994	−0.1809
$\beta_{\parallel}^{pvl-}$	0.000	−0.0680	−0.0617
$\beta_{\parallel}^{pvq}$	3.445	0.0023	0.0003
$\beta_{\parallel}^{zpvc}$	−1.039	−1.182	−1.438
$\beta_{\parallel}^{\text{vib-tot}}$	8.495	−1.847	−1.739
$\beta_{\parallel}^{\text{eq}}$ [a]	−17.70	−19.21	−21.68
$\beta_{\parallel}^{\text{tot}}$ [a]	−9.205	−21.06	−23.42
$\beta_{\parallel}^{\text{eq}}$ [b]	−17.38	−18.85	−21.28
$\beta_{\parallel}^{\text{tot}}$ [b]	−8.885	−20.70	−23.02
Expt.		-19.2 ± 0.9 [c]	-22.0 ± 0.9 [d]

[a]This work.
[b]Equilibrium geometry result from Ref. 53 and vibrational contributions from this work.
[c]From Ref. 56.
[d]From Ref. 57 rescaled in Ref. 2.

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TABLE VII. Total vibrational contributions to $\beta_{\parallel}(\omega,\omega)$ for formaldehyde calculated at external frequencies of ω=0.0, 0.0428, and 0.0656 a.u. Values are in atomic units.

	0.0			0.0428			0.0656		
	VCI[2]	VCI[3]	VCI[4]	VCI[2]	VCI[3]	VCI[4]	VCI[2]	VCI[3]	VCI[4]
$\beta_{\parallel}^{pvl+}$	−2.94	−2.71	−2.73	1.46	1.46	1.46	0.63	0.63	0.63
$\beta_{\parallel}^{pvl-}$	0.00	0.00	0.00	0.14	0.14	0.14	0.15	0.15	0.15
$\beta_{\parallel}^{pvq}$	4.53	4.75	4.74	0.01	0.01	0.01	0.00	0.00	0.00
$\beta_{\parallel}^{zpvc}$	−6.75	−6.74	−6.74	−8.03	−8.02	−8.02	−11.00	−10.98	−10.98
$\beta_{\parallel}^{\text{vib-tot}}$	−5.16	−4.70	−4.72	−6.42	−6.41	−6.41	−10.21	−10.20	−10.19
$\beta_{\parallel}^{\text{eq}}$	−49.84	−49.84	−49.84	−55.14	−55.14	−55.14	−64.16	−64.16	−64.16
$\beta_{\parallel}^{\text{tot}}$	−55.00	−54.54	−54.56	−61.56	−61.55	−61.55	−74.37	−74.36	−74.35

At optical frequencies the vibrational contributions are seen to be dominated by the ZPVC term and although this was also found for FH, it is becoming more pronounced for the water molecule. In the static limit the β^{pvl+} term dominates. For the water molecule the vibrational contributions to the total response at optical frequencies account for almost 10% and are thus non-negligible.

The values of $\beta_{\parallel}^{\text{tot}}$ calculated in this study are in reasonable agreement with the experimental ones. Our values are only slightly larger in magnitude. It should be noted that our results do not include the effect of triple excitations in the electronic part, although they have been found to be important.[53] We have therefore included these effects as obtained in the CC3 calculations of Ref. 53 in Table VI. The total combined electronic and vibrational first hyperpolarizabilities for water thus becomes −20.70 and −23.02 a.u. for frequencies of 0.0428 and 0.0656 a.u., respectively. These values agree even better with the experimental ones (-19.2 ± 0.9 and -22.0 ± 0.9 a.u., respectively) but are just outside the experimental error bars, which are again relatively large.

3. Formaldehyde

In Table VII we present the total rotationally averaged quadratic response function ($\beta_{\parallel}$) for formaldehyde. As was observed for the water molecule, the total vibrational contribution to the response at optical frequencies is determined largely by the ZPVC term. The PV quadratic response term is practically quenched at optical frequencies but gives a large contribution in the static limit. The PV linear response terms fall off somewhat slower for formaldehyde compared with water and hydrogen fluoride. The ZPVC behaves similar with the external frequency to what was observed for water and FH, i.e., the contribution increases in magnitude with increasing optical frequency. The total vibrational contributions are in this case seen to be larger than 10% and in fact larger (relative and absolute) for a frequency of 0.0656 a.u. as opposed to the static limit.

From Table VII it is evident that the convergence of the individual contributions with increasing level of mode-mode correlation is fast. Some variations are observed in going from VCI[2] to VCI[3]. Including also all configurations with four modes excited simultaneously has very limited effect on the results.

4. Pyrrole

The results obtained for the total quadratic response function for the pyrrole molecule are presented in Table VIII. The computation of the frequency-dependent property surfaces is a tremendous task for a system of the size of pyrrole. This primarily stems from the solution of the electronic response equations needed for constructing the electronic linear and quadratic response properties. A simple strategy for reducing the number of single point electronic structure calculations is to simply neglect mode-mode coupling in the property surfaces. In order to test the effect of mode-mode coupling, we present in Table VIII, for the static limit, the results obtained with and without mode-mode coupling in the property surfaces. We note that the dipole moment components are very simple to calculate and may be done with negligible cost when constructing the PES. For this reason, the coupled dipole moment surfaces are used in all cases. The results show some variations, about 15% for the $\beta_{\parallel}^{pvl+}$ contribution, which may be ascribed solely to the polarizability operators. The ZPVC term calculated without mode-mode coupling in the property surfaces is some 50% larger but only 0.6 a.u. in absolute terms in these sample calculations. Based on these observations, the frequency-dependent property surfaces are calculated without mode-mode coupling.

The results at the static limit show that the PV effects are very large and actually constitute more than 95% of the total hyperpolarizability. The contributions from the PV quadratic response functions are seen to be dominating. The linear symmetric response functions provide a contribution, which is a factor of 2 larger than the equilibrium geometry value,

TABLE VIII. Total vibrational contributions to $\beta_{\parallel}(\omega,\omega)$ for pyrrole calculated at external frequencies of ω=0.0, 0.0428, and 0.0656 a.u. Values are in atomic units.

	Coupling	No coupling		
	0.0	0.0	0.0428	0.0656
$\beta_{\parallel}^{pvl+}$	−40.46	−46.39	1.64	0.67
$\beta_{\parallel}^{pvl-}$	0.00	0.00	0.43	0.43
$\beta_{\parallel}^{pvq}$	−707.8	−707.8	0.00	0.00
$\beta_{\parallel}^{zpvc}$	1.36	1.94	1.93	2.41
$\beta_{\parallel}^{\text{vib-tot}}$	−746.9	−752.2	4.00	3.51
$\beta_{\parallel}^{\text{eq}}$	−19.43	−19.43	−21.73	−24.18
$\beta_{\parallel}^{\text{tot}}$	−766.3	−771.6	−17.73	−20.67

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and can clearly not be neglected. Averaging the first hyperpolarizability components over the vibrational ground state, i.e., the ZPVC results, gives minor but non-negligible contributions. The large vibrational contributions to the static first hyperpolarizability for pyrrole, being a rather large molecule, are very much in line with the observations by other groups, see Refs. 11, 12, 14, and 16.

The vibrational contributions to the static first hyperpolarizability of pyrrole have been studied by Alparone *et al.*[14] The present study overall confirms their findings, although our results are somewhat larger in magnitude. Reference 14 reports a β_{vec} value of 398.27 a.u., whereas we obtain a value of 746.9 a.u. including pair couplings in the property surfaces.

Switching to the results for $\beta_{\parallel}$ at optical frequencies, one observes a drastic decrease in the PV terms. At 0.0428 a.u., the PV linear symmetric response function ($\beta_{\parallel}^{pvl+}$) drops by an order of magnitude and the PV quadratic response contribution by as much as four orders of magnitude. The asymmetric term, however, becomes larger in magnitude and constitutes more than 10% of the total vibrational contribution at the two optical frequencies considered. It is worth to note that the PV linear asymmetric term becomes almost as large as the symmetric one for a frequency of 0.0656 a.u. The total vibrational contribution is around 15%–25%.

V. SUMMARY

We derived expressions for the total quadratic response of a molecular system in terms of electronic linear and quadratic response functions. Quadratic response theory was implemented for VCI wave functions. In combination with previous implementations, this allows the calculation of frequency-dependent third order properties, as e.g., the first hyperpolarizability. Sample calculations have been presented for hydrogen fluoride, water, formaldehyde, and pyrrole and compared with available experimental data.

Furthermore it has been demonstrated that the PV terms are non-negligible and that the PV contributions to the NLO properties primarily stem from the linear response terms, while the quadratic term tends to be negligible for all optical frequencies. In the static limit the contributions may be very large and arise primarily from the PV linear response functions including electronic ground state dipole and polarizability operators and, for the pyrrole molecule, from the PV quadratic response function.

New to our derivations is the emergence of a troublesome so-called asymmetric electronic linear response function. We investigated the effect of approximating the electronic asymmetric linear response function by the symmetric one multiplied by an appropriate scaling function derived from the electronic excitation energies. This approximate approach provided results very similar to those obtained using the true asymmetric linear response function. This may prove to be a cost efficient approximation for future work, since otherwise the evaluation of this term is difficult.

We also studied the effect of finite lifetimes of the vibrational excited states through the SOS expression, which has also been implemented. A troubling issue is that we have often found serious problems in converging the linear response equations for optical frequencies. The reason for these convergence problems is primarily believed to be the high density of vibrational states for optical frequencies. This in turn relies on two parameters: (i) the size of the system (a larger system is more likely to yield a higher density of states around a specific laser frequency) and (ii) the correlation level in the vibrational wave function with more Hartree products created for higher levels of mode-mode correlation. Addressing these complications is considered in continuation of this work.

The future perspectives include the formal derivation of the second hyperpolarizability and vibronic two-photon absorption matrix elements within the framework presented in this paper.

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