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Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.1627760](https://doi.org/10.1063/1.1627760)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Jensen, L., van Duijnen, P. T., & Snijders, J. G. (2003). A discrete solvent reaction field model for calculating frequency-dependent hyperpolarizabilities of molecules in solution. *Journal of Chemical Physics*, 119(24), 12998-13006. <https://doi.org/10.1063/1.1627760>

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Citation: *J. Chem. Phys.* **119**, 12998 (2003); doi: 10.1063/1.1627760

View online: <https://doi.org/10.1063/1.1627760>

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A discrete solvent reaction field model for calculating frequency-dependent hyperpolarizabilities of molecules in solution

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(Received 2 July 2003; accepted 29 September 2003)

We present a discrete solvent reaction field (DRF) model for the calculation of frequency-dependent hyperpolarizabilities of molecules in solution. In this model the solute is described using density functional theory (DFT) and the discrete solvent molecules are described with a classical polarizable model. The first hyperpolarizability is obtained in an efficient way using time-dependent DFT and the $(2n + 1)$ rule. The method was tested for liquid water using a model in which a water molecule is embedded in a cluster of 127 classical water molecules. The frequency-dependent first and second hyperpolarizabilities related to the electric field induced second harmonic generation (EFISH) experiment, were calculated both in the gas phase and in the liquid phase. For water in the gas phase, results are obtained in good agreement with correlated wave function methods and experiments by using the so-called shape-corrected exchange correlation (xc)-potentials. In the liquid phase the effect of using asymptotically correct functionals is discussed. The model reproduced the experimentally observed sign change in the first hyperpolarizability when going from the gas phase to the liquid phase. Furthermore, it is shown that the first hyperpolarizability is more sensitive to damping of the solvent-solute interactions at short range than the second hyperpolarizability. © 2003 American Institute of Physics. [DOI: 10.1063/1.1627760]

I. INTRODUCTION

Accurate predictions of molecular response properties, like the frequency-dependent (hyper)polarizability, in the condensed phase and in the gas phase are of great interest both from a theoretical and a technological point of view.¹⁻³ However, accurate calculations of molecular properties require a quantum mechanical treatment, which, due to high computational cost, are limited to small systems. Time-dependent density functional theory (TD-DFT) (Refs. 4-8) allows for the calculation of frequency-dependent response properties like electronic excitations and frequency-dependent (hyper)polarizabilities. The use of TD-DFT for calculating molecular response properties in the gas-phase has been shown to be accurate for small and medium size molecules, especially if one uses recently developed density functionals.⁹⁻¹⁸ Therefore, the extension of TD-DFT to treat also molecules in solution is of great interest.

The calculation of response properties of molecules in condensed phase is a fundamental and important theoretical challenge, which still remains problematic. Since the molecular properties like (hyper)polarizabilities are sensitive to the local environment, an accurate calculation of these properties could serve as a test for the molecular models used in describing intermolecular forces. The most successful methods divide the total system into two parts, one the molecular system of interest which is described with a quantum mechanical method and two the rest of the system which is

treated by a much simpler method, usually a classical description.¹⁹⁻³³ Among these methods are the combined quantum mechanical and classical mechanics models (QM/MM).²²⁻³³ In the QM/MM methods the solvent molecules are treated with a classical force field and the interactions between the solute and solvent are described with an effective operator, so the problem that remains is to find an accurate approximate representation of the solvent molecules and the solute-solvent interactions.³⁴

An example of such a QM/MM method is the discrete solvent reaction field model (DRF) which we recently developed.^{35,36} Although in this model the QM part is treated using density functional theory (DFT) it is not restricted to this approach. The permanent electronic charge distribution of the solvent molecules (MM) is modeled by point charges, while distributed atomic polarizabilities are included to model the solvent polarization arising from many-body interactions. The permanent point charges represent at least the permanent molecular dipole moment, and the distributed atomic polarizabilities the full molecular polarizability tensor. The QM/MM interactions are introduced into the Kohn-Sham equations through an effective operator and all interactions are solved self-consistently, which allows the solute to be polarized by the solvent. An important feature of the model is the inclusion of polarizabilities in the MM part which allows for the solvent molecules to be polarized by the solute and by interactions with other solvent molecules. The advantages of including polarizabilities in the MM part is that all parameters can be obtained from gas phase properties. Furthermore, it is expected that a distributed polarizabil-

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ity approach will give better results than an approach in which one models the molecular polarizability using only a single (anisotropic) polarizability per molecule, especially as the size of the solvent molecule increases.³⁷ Although standard DFT methods have problems describing van der Waals interactions, see e.g., Ref. 38, these problems are not present here since the van der Waals interactions are treated purely classical. The van der Waals interactions are typically treated using a Lennard-Jones (LJ) potential where the LJ parameters are taken from the classical force field or optimized to the particular QM/MM method.³⁹ However, it is not certain that optimizing the parameters on small complexes will improve the results in a QM/MM simulation⁴⁰ of a liquid. So far the DRF model has been applied to study the dipole and quadrupole moments³⁵ and linear response properties like vertical excitation energies and frequency-dependent polarizability³⁶ of a water molecule in aqueous solution.

Therefore, as a natural extension, we will apply the discrete solvent reaction field model to calculate the frequency-dependent hyperpolarizability of a molecule in solution within TD-DFT. This allows for the discrete representation of the solvent to be retained, and electron correlation of the QM part to be included in an efficient manner. The calculation of the frequency-dependent first hyperpolarizability will be achieved efficiently by the use of the $(2n+1)$ rule.⁴¹ Within a QM/MM approach the treatment of frequency-dependent hyperpolarizability has only been considered in one previous study using both correlated and uncorrelated wave function based methods.⁴² As in our previous study on dipole and quadrupole moments³⁵ and linear response properties³⁶ of water in aqueous solution we will adopt the same water structure for which the wave function QM/MM results exist.⁴² This will allow us to assess approximate exchange-correlation (xc) potentials for calculating molecular frequency-dependent hyperpolarizabilities in solution.

II. THEORY

A. The discrete reaction field model

In the QM/MM method the total (effective) Hamiltonian for the system is written as^{22–33}

$$\hat{H} = \hat{H}_{\text{QM}} + \hat{H}_{\text{QM/MM}} + \hat{H}_{\text{MM}}, \quad (1)$$

where \hat{H}_{QM} is the quantum mechanical Hamiltonian for the solute, $\hat{H}_{\text{QM/MM}}$ describes the interactions between solute and solvent, and \hat{H}_{MM} describes the solvent–solvent interactions. The discrete reaction field model is described in Ref. 35 within ground state DFT and in Ref. 36 within time-dependent DFT for the linear response properties and are therefore only briefly outlined here. Within the discrete reaction field model the QM/MM operator is given by

$$\hat{H}_{\text{QM/MM}} = \sum_i v^{\text{DRF}}(r_i, \omega) = \sum_i v^{\text{el}}(r_i) + \sum_i v^{\text{pol}}(r_i, \omega), \quad (2)$$

where i runs over all electrons in the QM system. The first term is the electrostatic operator describing the Coulombic

interactions between the QM system and the permanent charge distribution of the solvent molecules and is given by

$$v^{\text{el}}(r_i) = \sum_s \frac{q_s}{R_{si}} = \sum_s q_s T_{si}^{(0)}. \quad (3)$$

Here the zeroth order interaction tensor has been introduced and the index s runs over all atoms of the solvent molecules. The second term is the polarization operator given by

$$v^{\text{pol}}(r_i, \omega) = \sum_s \mu_{s,\alpha}^{\text{ind}}(\omega) \frac{R_{si,\alpha}}{R_{si}^3} = - \sum_s \mu_{s,\alpha}^{\text{ind}}(\omega) T_{si,\alpha}^{(1)}, \quad (4)$$

where $R_{si,\alpha}$ is a component of the distance vector and $\mu_s^{\text{ind}}(\omega)$ is the induced dipole at site s . For Greek indices the Einstein summation convention is employed. The polarization operator describes the many-body polarization of the solvent molecules, i.e., the change in the charge distribution of the solvent molecules due to interactions with the QM part and with other solvent molecules.

For a collection of atomic polarizabilities in an electric field the induced atomic dipole at site s is given, in linear response, by⁴³

$$\mu_{s,\alpha}^{\text{ind}}(\omega) = \alpha_{s,\alpha\beta} \left[F_{s,\beta}^{\text{init}}(\omega) + \sum_{t \neq s} T_{st,\beta\gamma}^{(2)} \mu_{t,\gamma}^{\text{ind}}(\omega) \right], \quad (5)$$

where $\alpha_{s,\alpha\beta}$ is a component of the atomic polarizability tensor at site s , which, for an isotropic atom, gives $\alpha_{s,\alpha\beta} = \delta_{\alpha\beta} \alpha_s$. Here we neglect the frequency-dependence of the classical part, i.e., the atomic polarizability is frequency independent, but the model can easily be extended to include also this effect.^{44,45} $F_{s,\beta}^{\text{init}}(\omega)$ is the initial electric field at site s and consists of the field arising from the frequency-dependent electronic charge distribution of the QM part, $F_{t,\beta}^{\text{QM,el}}(\omega)$, the field arising from the QM nuclei, $F_{t,\beta}^{\text{QM,nuc}}$, and the field arising from the point charges at the solvent molecules, $F_{t,\beta}^{\text{MM},q}$. The initial field does not include the electric field perturbing the QM part which means that the perturbing field can be identified as the local field felt by the QM molecule. This leads to the identification of the calculated properties as the solute properties, i.e., the (hyper)polarizability of the solute including the solvent effects but not corrected for the difference between the local field and the macroscopic field. For a discussion of these effects and corrections within the dielectric continuum model see, e.g., Ref. 46–48. The last term is the electric field from the other induced dipoles. It is well known that if the distance between two polarizable points become too small, the induced dipoles become infinite. In order to avoid this “polarizability catastrophe” we modified the dipole interaction tensor using smeared-out dipoles according to the model by Thole.⁴⁹ The induced dipole in Eq. (5) depends on the induced dipoles at the other sites, and therefore the equation should be solved self-consistently.

B. The frequency-dependent (hyper)polarizability

The total dipole moment of a molecule in the presence of a time-dependent electric field, $F_\beta = F_\beta^0 + F_\beta^\omega \cos(\omega t)$, can be expanded as a Taylor series in the applied electric field⁵⁰

$$\begin{aligned}\mu_\alpha &= \mu_\alpha^0 + \alpha_{\alpha\beta}(0;0)F_\beta^0 + \alpha_{\alpha\beta}(-\omega;\omega)F_\beta^\omega \cos(\omega t) \\ &+ \frac{1}{2}\beta_{\alpha\beta\gamma}(0;0,0)F_\beta^0 F_\gamma^0 + \frac{1}{4}\beta_{\alpha\beta\gamma}(0;\omega,-\omega)F_\beta^\omega F_\gamma^\omega \\ &+ \beta_{\alpha\beta\gamma}(-\omega;0,\omega)F_\beta^0 F_\gamma^\omega \cos(\omega t) \\ &+ \frac{1}{4}\beta_{\alpha\beta\gamma}(-2\omega;\omega,\omega)F_\beta^\omega F_\gamma^\omega \cos(2\omega t) + \dots, \quad (6)\end{aligned}$$

where $\alpha_{\alpha\beta}$ is the molecular polarizability and $\beta_{\alpha\beta\gamma}$ is the molecular first hyperpolarizability with (α,β,γ) designating Cartesian coordinates. The total dipole moment can be obtained from the trace of the dipole moment matrix, H^α , and the density matrix in the presence of the electric field, $P(F)$,

$$\mu_\alpha = -\text{Tr}[H^\alpha P(F)]. \quad (7)$$

We can expand the density matrix in a Taylor series,

$$P = P^0 + P^\beta F_\beta + \frac{1}{2!} P^{\beta\gamma} F_\beta F_\gamma + \dots, \quad (8)$$

where P^0 is the unperturbed density matrix, P^β is the linear response and $P^{\beta\gamma}$ is the quadratic response. Inserting this expansion into Eq. (7) and comparing with Eq. (6) allows us to identify the dipole moment, the frequency-dependent polarizability, and the frequency-dependent first hyperpolarizability as

$$\mu_\alpha = -\text{Tr}[H^\alpha P^0], \quad (9)$$

$$\alpha_{\alpha\beta}(-\omega;\omega) = -\text{Tr}[H^\alpha P^\beta(\omega)], \quad (10)$$

$$\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_a,\omega_b) = -\text{Tr}[H^\alpha P^{\beta\gamma}(\omega_a,\omega_b)], \quad (11)$$

where $\omega_\sigma = \omega_a + \omega_b$. In the following we will present how to obtain the linear and quadratic response properties using the $(2n+1)$ rule.

C. Linear response of the density matrix

In our previous work³⁶ we showed, using time-dependent response theory,⁴⁻⁸ how to obtain the first-order change in the density matrix, $P^\beta(\omega)$, from a set of linear equations,

$$P_{st}(\omega) = \frac{\Delta n_{st}}{(\epsilon_s - \epsilon_t) - \omega} \delta v_{st}^{\text{eff}}(\omega), \quad (12)$$

where Δn_{st} is the difference in occupation numbers, i.e., 1 for $st=ai$ and -1 for $st=ia$, where a denote virtual orbitals and i denote occupied orbitals. This equation now corrects a misprint in Eqs. (21) and (25) of our previous paper.³⁶ The change in the effective potential, $\delta v_{st}^{\text{eff}}$, is dependent on the first order change in the density and is given by

$$\begin{aligned}\delta v_{st}^{\text{eff}}(\omega) &= \delta v_{st}^{\text{per}}(\omega) + \int dr \phi_s^*(r) [v_{\text{Coul}}[\delta\rho](r,\omega) \\ &+ v_{\text{xc}}[\delta\rho](r,\omega) + v^{\text{DRF}}[\delta\rho](r,\omega)] \phi_t(r),\end{aligned} \quad (13)$$

where the Coulomb term is given by

$$v_{\text{Coul}}[\delta\rho](r,\omega) = \int dr' \frac{\delta\rho(r',\omega)}{|r-r'|}, \quad (14)$$

the xc part in the adiabatic approximation by

$$v_{\text{xc}}[\delta\rho](r,\omega) = \int dr' \frac{\delta v_{\text{xc}}(r')}{\delta\rho(r')} \delta\rho(r',\omega), \quad (15)$$

and the contribution from the DRF operator by

$$v^{\text{DRF}}[\delta\rho](r_i,\omega) = -\sum_s \mu_{s,\alpha}^{\text{ind}}[\delta\rho](\omega) T_{si,\alpha}^{(1)}. \quad (16)$$

The DRF contribution arises from the induced dipoles in the MM part due to the first-order change in the QM charge distribution. Since the effective potential in Eq. (13) depends on the first-order density matrix through the potentials $v_{\text{Coul}}[\delta\rho](r,\omega)$, $v_{\text{xc}}[\delta\rho](r,\omega)$, and $v^{\text{DRF}}[\delta\rho](r_i,\omega)$ a self-consistent solution of Eq. (12) is required.

D. Quadratic response of the density matrix using the $(2n+1)$ rule

In a manner similar to the linear response a set of equations for the solution of the higher order density response can be constructed.^{16-18,41,51} However, a more efficient approach is to take advantage of the $(2n+1)$ rule which allows for the quadratic response properties to be rewritten in terms of quantities obtained from the solution of the first order response equations. Within TD-DFT van Gisbergen *et al.* have shown how this is done for the frequency-dependent first hyperpolarizability⁴¹ in an approach similar to the TD-HF approach of Karna and Dupuis.⁵² Here we will present the results obtained by van Gisbergen⁴¹ since the inclusion of the DRF operator will not affect the structure of these equations.

The frequency-dependent first hyperpolarizability can be rewritten using the $(2n+1)$ rule as⁴¹

$$\begin{aligned}\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_a,\omega_b) &= -\text{Tr}[H^\alpha P^{\beta\gamma}(\omega_a,\omega_b)] \\ &= \hat{p}\{(\alpha,\omega_\sigma),(\beta,\omega_a),(\gamma,\omega_b)\} \\ &\quad \times \text{Tr}[nU^\alpha(-\omega_\sigma)[G^\beta(\omega_a),U^\gamma(\omega_b)]_-] \\ &\quad + \text{Tr}[g_{\text{xc}}(\omega_a,\omega_b)P^\alpha(-\omega_\sigma)P^\beta(\omega_a)P^\gamma(\omega_b)],\end{aligned} \quad (17)$$

where $[G^\beta(\omega_a),U^\gamma(\omega_b)]_-$ denotes the commutator of $G^\beta(\omega_a)$ and $U^\gamma(\omega_b)$, and \hat{p} the sum of all permutations of $(\alpha,-\omega_\sigma)$, $(\beta,-\omega_a)$, and $(\gamma,-\omega_b)$. The $G^\alpha(\omega_a)$ matrix is the first-order KS matrix⁴¹ and is given by

$$\begin{aligned}G_{pg}^\alpha(\omega) &= \int dr \phi_p(r) [v_{\text{per}}^\alpha + v^{\text{Coul}}[\delta\rho^\alpha(\omega)] + v_{\text{xc}}(r) \\ &\quad \times [\delta\rho^\alpha(\omega)](r) + v^{\text{DRF}}[\delta\rho^\alpha(\omega)](r)] \phi_q(r)\end{aligned} \quad (18)$$

which is identical to the effective potential matrix, $\delta v^{\text{eff}}(\omega_a)$, in Eq. (13) due to the α -component of the perturbation. The first-order transformation matrix, $U^\alpha(\omega)$, is given by

$$U_{pq}^\alpha(\omega) = \frac{G_{pg}^\alpha(\omega)}{\epsilon_q^{(0)} - \epsilon_p^{(0)} - \omega} \quad (19)$$

and is only nonzero for the occupied-virtual block.⁴¹ The last term in Eq. (17) is an additional term in the DFT expression which is not present in the TDHF case and is given by

$$\begin{aligned} & \text{Tr}[g_{xc}(\omega_a, \omega_b) P^\alpha(-\omega_\sigma) P^\beta(\omega_a) P^\gamma(\omega_b)] \\ &= \int dr \int dr' \int dr'' g_{xc}(r, r', r'', \omega_a, \omega_b) \\ & \quad \times \delta\rho^\alpha(r, -\omega_\sigma) \delta\rho^\beta(r', \omega_a) \delta\rho^\gamma(r'', \omega_b), \end{aligned} \quad (20)$$

where the xc kernel, g_{xc} , has been introduced,

$$g_{xc}(r, r', r'', \omega_a, \omega_b) = \frac{\delta^2 v_{xc}(r)}{\delta\rho(r', \omega_a) \delta\rho(r'', \omega_b)} \Big|_{\rho(0)}. \quad (21)$$

Usually the adiabatic approximation is invoked for this kernel,

$$g_{xc}(r, r', r'', \omega_a, \omega_b) \approx g_{xc}(r, r', r'', 0, 0). \quad (22)$$

E. Implementation

The DRF model has been implemented into a local version of the Amsterdam Density Functional (ADF) program package.^{53,54} The extension to the TD-DFT part has been implemented into the RESPONSE module of the ADF.^{41,55,56} In the RESPONSE module the functional derivative of the xc-potential in Eqs. (15) and (21) is restricted to the Adiabatic LDA (ALDA) xc-potential. The linear equations for the first-order density matrix in Eq. (12) is solved using an efficient iterative algorithm,⁵⁵ and, for that reason, the DRF response operator, Eq. (16), are calculated by solving a set of linear equations like in Eq. (5). In ADF the KS equations and the linear response equations are solved by numerical integration and the numerical integration grid is chosen on the basis of the quantum part alone. Therefore, care must be taken when evaluating the DRF operator if the integration points are close to a classical atom. In order to avoid numerical instabilities we introduce a damping of the operators at small distances. This is done by replacing the point charge by a Gaussian charge distribution with a unit width and the point dipoles are also smeared out in a similar manner.^{35,36,45}

III. COMPUTATIONAL DETAILS

The water structure used in this work, taken from Ref. 57, consists of 128 rigid water molecules where one molecule is treated quantum mechanically. The total structure was obtained from a MD simulation using a polarizable force field.⁵⁸ Details about the simulation can be found in Refs. 59, 60 and will be summarized here for consistency. The average geometry is obtained from a simulation of a box containing 128 water molecules utilizing periodic boundary conditions with a spherical cut-off distance of 10.0 Å, at a temperature of 298 K, and a pressure of 0.103 MPa. After equilibration, the average geometry was obtained from a Boltzmann sampling of 8000 trajectories started with different initial velocity distributions and a simulation time of 20 ps for each trajectory. The intramolecular geometry of the water molecules was that as in the gas phase, i.e., $R_{\text{O-H}} = 0.9572$ Å and $\angle_{\text{HOH}} = 104.49^\circ$. The solute water molecule was placed in the xz -plane with the z -axis bisecting the H–O–H angle.

The basis set used in this work consists of a large even-tempered basis set of Slater-type orbitals with orbital exponent $\zeta = \alpha\beta^i$, $i = 1, \dots, n$ (details given in Ref. 36). Different

xc potentials have been tested: the local density approximation (LDA), Becke–Lee–Yang–Parr (BLYP),^{61,62} the Becke–Perdew (BP),^{61,63} the van Leeuwen–Baerends (LB94),⁶⁴ the statistical averaging of (model) orbital potentials (SAOP),^{12,65,66} and the potential obtained from the gradient-regulated asymptotic connection procedure applied to the BP potentials (BP-GRAC).^{14,15} The BLYP and BP are examples of typical generalized gradient approximations (GGAs) potentials and the LB94 is an example of an asymptotically correct potential. Whereas SAOP and BP-GRAC belong to a class of shape-corrected potentials, which yield the correct asymptotic behavior. The BP-GRAC potential sets the HOMO level at the first ionization potential (IP) and therefore requires the IP as input. The SAOP xc-potential requires no additional input and the energy of the HOMO corresponds well with the IP.^{15,67} For this reason the IP needed as input for the BP-GRAC xc-potential is taken from the SAOP gas-phase calculation, i.e., IP=0.45 a.u.

The parameters needed for the solvent molecules, i.e., point charges and atomic polarizabilities, were taken from Ref. 35. The point charges are $q_{\text{H}} = 0.3345$ a.u. and $q_{\text{O}} = -0.6690$ a.u. which generate a molecular dipole moment of 1.88 Debye. The atomic polarizabilities are $\alpha_{\text{H}} = 0.0690$ a.u. and $\alpha_{\text{O}} = 9.3005$ a.u. which reproduced the molecular polarizability tensor with a mean polarizability of 9.62 a.u. and a polarizability anisotropy of 0.52 a.u. The screening parameter, $a = 2.1304$, was taken from Ref. 68.

From the analytically calculated frequency-dependent first hyperpolarizability in Eq. (17) we can obtain the second hyperpolarizability by using finite field differentiation. We have calculated the frequency-dependent second hyperpolarizability associated with the electric field induced second harmonic generation (EFISH) experiments by finite field differentiation of the second harmonic generation (SHG) first hyperpolarizability as

$$\begin{aligned} & \gamma_{\alpha\beta\gamma\delta}(-2\omega; \omega, \omega, 0) \\ &= \frac{\beta_{\alpha\beta\gamma}^F(-2\omega; \omega, \omega) - \beta_{\alpha\beta\gamma}^0(-2\omega; \omega, \omega)}{F_\delta}, \end{aligned} \quad (23)$$

where the field strength $F_\delta = 0.001$ a.u. was used. We will in this work use atomic units (a.u.) but the conversion factor to cgs units are⁶⁹ for β : 1 a.u. = 8.6392×10^{-33} esu and for γ : 1 a.u. = 5.0367×10^{-40} esu.

IV. RESULTS

A. The first hyperpolarizability

In Table I we present the static and frequency-dependent first hyperpolarizability, $\beta(-2\omega; \omega, \omega)$, at frequencies $\omega = 0.0428, 0.0570, 0.0856$ a.u. ($\lambda = 1064, 800, 532$ nm, respectively) of water in the gas phase calculated with the different xc potentials. The mean first hyperpolarizability, $\bar{\beta}$, defined as⁶⁹

$$\bar{\beta} = \frac{1}{5} \sum_{\alpha} (\beta_{z\alpha\alpha} + \beta_{\alpha z\alpha} + \beta_{\alpha\alpha z}) = \frac{3}{5} (\beta_{zzz} + \beta_{zyy} + \beta_{zxx}) \quad (24)$$

TABLE I. Static and frequency dependent SHG first hyperpolarizability, $\beta(-2\omega; \omega, \omega)$, for water in the gas phase. All results are in a.u.

	LDA	BLYP	BP	LB94	SAOP	BP-GRAC	HF ^a	MC-SCF ^a	CCSD ^b	CCSD(T) ^c
β_{zzz}	-19.70	-20.65	-17.79	-13.11	-13.69	-14.98	-7.30	-10.8	-13.97	-13.8
β_{zyy}	-9.01	-8.35	-7.51	-4.47	-4.78	-5.96	-1.23	-4.27	-5.66	-5.5
β_{zxx}	-11.80	-13.38	-11.59	-10.03	-10.28	-10.41	-9.36	-8.90	-9.92	-9.8
$\bar{\beta}$	-24.31	-25.43	-22.13	-16.57	-17.25	-18.81	-10.73	-14.38	-17.73	-17.5
$\omega = 0.0428$										
β_{zzz}	-21.97	-23.16	-19.71	-14.21	-14.92	-16.38	-7.81	-11.6	-15.12	
β_{zyy}	-10.08	-9.32	-8.33	-4.82	-5.18	-6.49	-1.25	-4.54	-6.07	
β_{zxx}	-12.86	-14.69	-12.57	-10.69	-10.94	-11.17	-9.83	-9.41	-10.53	
$\bar{\beta}$	-26.95	-28.30	-24.37	-17.83	-18.62	-20.42	-11.33	-15.33	-19.03	
$\Delta\bar{\beta}_{\text{disp}}^d$	10.9%	11.3%	10.1%	7.6%	7.9%	8.6%	5.6%	6.6%	7.3%	
$\omega = 0.0570$										
β_{zzz}	-24.02	-25.44	-21.43	-15.16	-15.99	-17.60	-8.25	-12.4		
β_{zyy}	-11.04	-10.17	-9.04	-5.11	-5.52	-6.95	-1.26	-4.76		
β_{zxx}	-13.80	-15.83	-13.44	-11.25	-11.55	-11.83	-10.2	-9.84		
$\bar{\beta}$	-29.32	-30.86	-26.35	-18.91	-19.84	-21.83	-11.83	-16.20		
$\Delta\bar{\beta}_{\text{disp}}^d$	20.6%	21.4%	19.1%	14.1%	15.0%	16.1%	10.3%	12.7%		
$\omega = 0.0856$										
β_{zzz}	-32.01	-34.44	-27.97	-18.55	-19.85	-22.06	-9.73	-15.0		
β_{zyy}	-14.63	-13.23	-11.62	-6.10	-6.70	-8.54	-1.26	-5.69		
β_{zxx}	-17.39	-20.28	-16.67	-13.20	-13.70	-14.17	-11.5	-11.3		
$\bar{\beta}$	-38.42	-40.77	-33.76	-22.71	-24.15	-26.86	-13.49	-19.19		
$\Delta\bar{\beta}_{\text{disp}}^d$	58.0%	60.3%	52.6%	37.1%	40.0%	42.8%	25.7%	33.4%		

^aResults from Ref. 42.^bResults from Ref. 70.^cResults from Ref. 71.^d $\Delta\bar{\beta}_{\text{disp}} = (\bar{\beta}(-2\omega; \omega, \omega) - \bar{\beta}(0; 0, 0)) / \bar{\beta}(0; 0, 0)$.

is also presented in Table I. The last equality is only valid in the static case or when Kleinman symmetry is adopted as is done in this work. The results are compared with results obtained from different wave function methods, i.e., HF,⁴² MC-SCF,⁴² CCSD,⁷⁰ and CCSD(T) results.⁷¹

From the results in Table I it is clear that the LDA/GGA (BLYP and BP) functionals overestimate the first hyperpolarizability as compared to the accurate CCSD and CCSD(T) wave function results. The asymptotically correct (AC) xc-potentials, LB94, SAOP, and BP-GRAC, all produce numbers in good agreement with the CCSD and CCSD(T) results. The overestimation of the first hyperpolarizability using LDA and GGAs (BLYP and BP) and the improvement upon this using AC potentials are well established for small molecules.^{12,15,72,73} Comparing the HF and MC-SCF results with the CCSD/CCSD(T) results we see that the results are underestimated, especially the HF results are underestimated illustrating the importance of electron correlations. Furthermore, comparing the frequency-dispersion of the mean first hyperpolarizability, we see that the increase in the hyperpolarizability, $\Delta\bar{\beta}_{\text{disp}}$, with increasing frequency is considerably larger with LDA/GGA than with the AC potentials and the HF and MC-SCF wave function results. The AC potentials predict a larger frequency-dispersion increase than HF and MS-SCF. From the results in Table I it is also seen that the frequency-dispersion is significant even for the lowest frequencies. It is therefore important to take this into account.

The static and frequency-dependent first hyperpolarizability of a water molecule in a cluster of 127 classical water molecules are presented in Table II. The frequencies used are

the same as in the gas phase and the results are compared with results for the same water cluster obtained using the HF/MM (Ref. 42) and the MC-SCF/MM (Ref. 42) method. Also presented is the solvation shift, $\Delta\bar{\beta}_{\text{solv}}$, i.e., the relative change in the first hyperpolarizability upon solvation. Due to the symmetry of the water cluster components other than the ones presented in Table II are also nonzero but these components have not been presented, since these components should tend to zero, by considering more solvent configurations, thereby creating a more realistic isotropic solvent environment by averaging over the different solvent configurations.

First it is noted that all methods predict a sign change for the first hyperpolarizability in going from the gas phase to the liquid phase. This sign shift is theoretically well established for methods containing some discrete water molecules in the description.^{42,74-77} As in the gas phase, the LDA/GGA results are larger than those from the AC potentials, but now the MC-SCF/MM results are the largest. The HF/MM results are also larger than the results from the AC potentials. However, the main difference between the wave function results and the DFT results is in $\Delta\bar{\beta}_{\text{solv}}$. The wave function methods predict a shift of $\sim 180\% - 200\%$, whereas the DFT methods predict a lower solvation shift of $\sim 120\% - 150\%$. Part of this difference is not due to differences between the wave function methods and DFT, but it is due to the inclusion of the damping of the DRF operator at short distances. To illustrate this we calculated the mean first hyperpolarizability, using the BP-GRAC xc-potential without the damping of the DRF operator, which increases the first hyperpolarizability

TABLE II. Static and frequency dependent SHG first hyperpolarizability, $\beta(-2\omega; \omega, \omega)$, for water in a cluster of 127 classical water molecules. All results are in a.u.

	LDA	BLYP	BP	LB94	SAOP	BP-GRAC	HF ^a	MC-SCF ^a
β_{zzz}	10.85	12.83	10.82	4.84	6.51	8.33	9.87	14.9
β_{zyy}	6.68	9.03	7.50	3.57	4.41	5.775	6.45	8.21
β_{zxx}	0.79	0.81	0.14	-2.61	-1.89	-0.78	-1.82	0.56
$\bar{\beta}$	10.99	13.60	11.08	3.48	5.42	7.99	8.70	14.20
$\Delta\bar{\beta}_{\text{solv}}^{\text{b}}$ $\omega = 0.0428$	145.2%	153.5%	150.1%	121.0%	131.4%	142.5%	181.1%	198.7%
β_{zzz}	11.63	13.85	11.58	5.05	6.87	8.79	10.4	15.8
β_{zyy}	7.30	10.05	8.24	3.81	4.74	6.20	6.90	8.88
β_{zxx}	1.05	1.10	0.33	-2.66	-1.89	-0.71	-1.82	0.72
$\bar{\beta}$	11.99	15.00	12.09	3.72	5.83	8.57	9.29	15.24
$\Delta\bar{\beta}_{\text{solv}}^{\text{b}}$ $\omega = 0.0570$	144.5%	153.0%	149.6%	120.9%	131.3%	142.0%	182.0%	199.4%
β_{zzz}	12.30	14.74	12.24	5.22	7.17	9.18	10.8	16.5
β_{zyy}	7.84	10.99	8.89	4.02	5.03	6.57	7.27	9.47
β_{zxx}	1.29	1.37	0.50	-2.70	-1.88	-0.69	-1.81	0.86
$\bar{\beta}$	12.86	16.26	12.98	3.92	6.19	9.04	9.76	16.10
$\Delta\bar{\beta}_{\text{solv}}^{\text{b}}$ $\omega = 0.0856$	143.9%	152.7%	149.3%	120.7%	131.2%	141.4%	182.5%	199.4%
β_{zzz}	14.66	18.00	14.58	5.77	8.16	10.46	12.1	19.2
β_{zyy}	9.90	14.75	11.44	4.72	6.02	7.87	8.56	11.7
β_{zxx}	2.19	2.42	1.16	-2.82	-1.82	-0.36	-1.79	1.41
$\bar{\beta}$	16.05	21.10	16.31	4.60	7.42	10.78	11.32	19.39
$\Delta\bar{\beta}_{\text{solv}}^{\text{b}}$	141.8%	151.8%	148.3%	120.3%	130.7%	140.1%	183.9%	201.0%

^aResults from Ref. 42.^b $\Delta\bar{\beta}_{\text{solv}} = (\bar{\beta}_{\text{liquid}} - \bar{\beta}_{\text{gas}}) / \bar{\beta}_{\text{gas}}$.

from $\bar{\beta} = 7.99$ a.u. to $\bar{\beta} = 11.92$ a.u. in closer agreement with the MC-SCF results. This indicates that the damping, although not optimized to treat this, mimics the short range repulsion due to the overlapping charge densities of the QM part and the MM part. The damping is dependent on the width of the Gaussian charge distribution, which in this work was taken to be unit (a.u.). However, both a slightly smaller width⁷⁸ and slightly larger width⁷⁹ have been suggested. Although further investigation of optimizing this damping to treat the short range repulsion should be carried out, it is expected to be more realistic to retain it in its present form than to ignore it completely. Similar approaches of employing screened charge interactions has also been used in other QM/MM studies.^{29,78-81}

Furthermore, from the results in Table II, we see that $\Delta\bar{\beta}_{\text{solv}}$ is almost independent of the frequency-dispersion, although the DFT methods predict a slight decrease in the solvation shift with increasing frequency and the wave function methods predict a slight increase with increasing frequency. This apparent frequency independence of $\Delta\bar{\beta}_{\text{solv}}$ could result from the neglect of the frequency-dependence of the classical environment in Eq. (5). Other theoretical models,⁷⁵⁻⁷⁷ where the molecular properties are calculated at the MP2 level of theory in the presence of a field from effective point charges representing the discrete solvent environment, in general predict a larger mean first hyperpolarizability ~ 25 a.u. (in the gas phase ~ -18 a.u.), but the results are strongly dependent on the actual representation of the local environment.⁷⁵⁻⁷⁷

B. The second hyperpolarizability

In Table III the static and frequency-dependent EFISH second hyperpolarizability, $\gamma(-2\omega; \omega, \omega, 0)$, at the frequency $\omega = 0.0428$ a.u. ($\lambda = 1064$ nm) of water in the gas phase calculated using different xc potentials is presented. The mean second hyperpolarizability, $\bar{\gamma}$, defined as⁶⁹

$$\begin{aligned} \bar{\gamma} &= \frac{1}{15} \sum_{\alpha\beta} \gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\alpha\beta} + \gamma_{\alpha\beta\beta\alpha} \\ &= \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} \\ &\quad + 2\gamma_{zzxx} + 2\gamma_{xxyy} + 2\gamma_{yyzz}) \end{aligned} \quad (25)$$

is also presented, where again the last equality assumes Kleinman symmetry. The results are compared with HF (Ref. 71) and CCSD(T) (Ref. 71) wave function results. As was the case for the first hyperpolarizability, the second hyperpolarizability is overestimated by as much as a factor of 2 using LDA/GGA as compared with the results from the AC potentials. Comparing with the wave function results we see that there is good agreement between the BP-GRAC results and the CCSD(T) results, and that HF considerably underestimates by nearly a factor of two. Also, for the second hyperpolarizability the frequency-dispersion, $\Delta\bar{\gamma}_{\text{disp}}$, is overestimated by a factor of about 2 using LDA/GGA as compared with the results from the AC potentials.

The static and frequency-dependent EFISH second hyperpolarizabilities for a water molecule in a cluster of 127

TABLE III. Static and frequency dependent EFISH second hyperpolarizability, $\gamma(-2\omega; \omega, \omega, 0)$ for water in the gas phase. All results are in a.u.

	LDA	BLYP	BP	LB94	SAOP	BP-GRAC	HF ^a	CCSD(T) ^a
γ_{xxxx}	1425.2	1586.7	1386.2	706.35	786.47	880.23	569	836
γ_{yyyy}	5301.8	6425.7	5163.9	1666.0	2080.6	2793.9	1422	2650
γ_{zzzz}	2573	2545	2222	1103	1316	1553	907	1481
γ_{zzxx}	1275.4	1511.2	1214.4	435.01	526.33	468.24	287	439
γ_{xxyy}	1366.5	1567.2	1268.4	470.51	578.3	683.9	338	633
γ_{yyzz}	1361.9	1526.6	1244	473.9	580.1	751.6	389	711
$\bar{\gamma}$	3461.5	3953.5	3245.1	1246.8	1510.5	1806.9	985	1706
$\omega = 0.0428$								
γ_{xxxx}	1577.2	1768.7	1531.5	752.38	842.05	944.55		
γ_{yyyy}	6404.7	7897.0	6213.4	1849.9	2342.0	3170.5		
γ_{zzzz}	2913	2881	2504	1197	1439	1702		
γ_{zzxx}	1614.6	1954.1	1528.0	495.78	608.61	518.41		
γ_{xxyy}	1581.2	1827.4	1460.0	514.2	637.8	753.5		
γ_{yyzz}	1691	1920.6	1533.1	533.4	661.9	872.7		
$\bar{\gamma}$	4133.7	4790.2	3858.2	1377.2	1687.9	2021.3		
$\Delta \bar{\gamma}_{\text{disp}}^b$	19.4%	21.2%	18.9%	10.5%	11.7%	11.9%		

^aResults from Ref. 71.^b $\Delta \bar{\gamma}_{\text{disp}} = (\bar{\gamma}(-2\omega; \omega, \omega, 0) - \bar{\gamma}(0; 0, 0, 0)) / \bar{\gamma}(0; 0, 0, 0)$.

classical water molecules calculated using different xc-potentials are presented in Table IV. The frequency used for the EFISH second hyperpolarizability is the same as in the gas phase, i.e., $\omega = 0.0428$ a.u. ($\lambda = 1064$ nm). Also presented in Table IV is the solvation shift, $\Delta \bar{\gamma}_{\text{solv}}$. Again, LDA/GGA results overestimate by a factor of 2 the results obtained using the AC potentials. In comparison with the solvation shift for the first hyperpolarizability the solvation shift in the second hyperpolarizability is much smaller for all xc-potentials. The main reason for this small difference in $\Delta \bar{\gamma}_{\text{solv}}$ predicted by LDA/GGA and the AC potentials is the different behavior of the individual tensor components upon solvation. That the xc-potentials predict different behavior upon solvation can be illustrated by considering the solvation shift in γ_{yyyy} , which is $\sim 29\%$ for LDA but only $\sim 19\%$ for BP-GRAC. We also see that $\Delta \bar{\gamma}_{\text{solv}}$ is more sensitive to the

frequency-dispersion than was the case for the first hyperpolarizability, and that an increase in frequency gives a decrease in the solvation shift. The effect of damping the DRF operator was found to be smaller for the second hyperpolarizability than for the first hyperpolarizability, e.g., the static mean second hyperpolarizability calculated with BP-GRAC increased from $\bar{\gamma} = 1908.5$ a.u. to $\bar{\gamma} = 1967.8$ a.u. by ignoring the damping.

Previous results calculated at the MP2 level of theory⁷⁷ for the static mean second hyperpolarizability of water in the liquid phase gave $\bar{\gamma} = 2417$ a.u. [in the gas phase $\bar{\gamma} = 1654$ a.u. (Ref. 77)]. This result was obtained by calculating the second hyperpolarizability in the presence of an average electric field representing the discrete molecular solvent environment. The solvation shift both for the first and second hyperpolarizabilities predicted in that work is found to be larger than what we predict in this work.

TABLE IV. Static and frequency dependent EFISH second hyperpolarizability, $\gamma(-2\omega; \omega, \omega, 0)$ for water in a cluster of 127 classical water molecules. All results are in a.u.

	LDA	BLYP	BP	LB94	SAOP	BP-GRAC
γ_{xxxx}	1437.1	1693.0	1325.3	679.4	761.0	821.5
γ_{yyyy}	6479.9	7742.3	6309.1	2002.3	2509.9	3246.8
γ_{zzzz}	2473.0	2827.0	2276.0	1141.2	1345.7	1505.2
γ_{zzxx}	757.7	921.8	691.0	353.0	408.9	453.2
γ_{xxyy}	1479.8	1744.1	1388.2	487.6	596.4	747.2
γ_{yyzz}	1439.0	1704.4	1368.6	525.9	640.1	784.1
$\bar{\gamma}$	3548.6	4200.58	3361.2	1311.2	1581.5	1908.5
$\Delta \bar{\gamma}_{\text{solv}}^a$ 0.0428	2.5%	6.2%	3.6%	5.2%	4.7%	5.6%
γ_{xxxx}	1592.3	1888.0	1465.0	721.3	812.7	877.3
γ_{yyyy}	7821.4	9531.4	7593.9	2226.5	2830.2	3670.2
γ_{zzzz}	2762.0	3182.0	2532.0	1229.8	1460.2	1629.4
γ_{zzxx}	854.8	1048.5	776.1	382.7	446.6	494.4
γ_{xxyy}	1697.3	2023.4	1585.2	528.7	652.0	818.5
γ_{yyzz}	1754.0	2129.0	1661.9	586.9	724.4	892.6
$\bar{\gamma}$	4157.6	5000.6	3927.5	1434.8	1749.8	2117.6
$\Delta \bar{\gamma}_{\text{solv}}^a$	5.4%	4.4%	1.8%	4.2%	3.7%	4.8%

^a $\Delta \bar{\gamma}_{\text{solv}} = (\bar{\gamma}_{\text{liquid}} - \bar{\gamma}_{\text{gas}}) / \bar{\gamma}_{\text{gas}}$.

C. Comparison with experiment

In the gas phase there have been two EFISH experiments from which the first and second hyperpolarizability of water have been determined; one at $\omega = 0.0428$ a.u. ($\lambda = 1064$ nm) (Ref. 82) and one at $\omega = 0.0656$ a.u. ($\lambda = 694.3$ nm).⁸³ In the EFISH experiment the measured quantity is⁸²

$$\Gamma(-2\omega; \omega, \omega, 0) = \bar{\gamma}(-2\omega; \omega, \omega, 0) + \frac{\mu \bar{\beta}(-2\omega; \omega, \omega)}{3kT} \quad (26)$$

from which the individual contributions can be extracted if one knows the dipole moment μ by performing the experiment at different temperatures. As discussed and clarified by Willetts *et al.*,⁵⁰ different conventions are often used in experiments and in calculations. It is therefore important to bring all results to the same convention before comparing. (For the definition of the different conventions, see Ref. 50.)

In this work the Taylor series (**T**) convention is used and all values are converted into this convention (see Ref. 50 for details). For clarity all details of the conversion are reported. The first experiment at $\omega=0.0656$ a.u. (Ref. 83) reported a value of $\bar{\beta} = -94 \pm 4 \times 10^{-33}$ esu = -11 ± 0.5 a.u. measured in the **B** convention. Converting this to the **T** convention gives $\bar{\beta} = (-11 \pm 0.5) \times 2 = -22 \pm 1$ a.u. For the second hyperpolarizability the reported value⁸³ is $\bar{\gamma} = 194 \pm 10 \times 10^{-39}$ esu = 385 ± 20 a.u. in the **B** convention and converting it to the **T** convention gives $\bar{\gamma} = (385 \pm 20) \times 6 = 2310 \pm 120$ a.u. The second experiment at $\omega=0.0428$ a.u. (Ref. 82) reported $\bar{\beta} = -19.2 \pm 0.9$ a.u. and $\bar{\gamma} = 1800 \pm 150$ a.u., both values reported in the **T** convention. Comparing these results with the calculated results for the first hyperpolarizability in Tabel I and the second hyperpolarizability in Table III, we find good agreement with the SAOP, BP-GRAC, CCSD, and CCSD(T) results, showing the ability of these methods to describe the first and second hyperpolarizability of water in the gas phase.

For liquid water there has been one EFISH experiment at $\omega=0.0428$ a.u.⁸⁴ Reported was a value of $\Gamma = 1.44 \times 10^{-36}$ esu = 2859 a.u. in the **X** convention which, converting to the **T** convention, gives $\Gamma = 2859 \times 4 = 11436$ a.u. The value was measured relative to a reference standard for which a quartz crystal was used with a value of $d_{11} = 0.8 \times 10^{-9}$ esu = 0.335 pm/V. However, the currently accepted value for quartz is $d_{11} = 0.30$ pm/V.^{85,86} In order to extract the contribution from the first hyperpolarizability they used an estimate for the second hyperpolarizability of $\bar{\gamma} = 0.3 \times 10^{-36}$ esu = 595.6 a.u. in the **X** convention. Converting this to the **T** convention and correcting for the difference in reference values of quartz, gives $\bar{\gamma} = 595.6 \times 4 \times 0.30 / 0.335 = 2133.6$ a.u. This value is in good agreement with our result obtained with the BP-GRAC potential. Furthermore, an estimate of the dipole moment in liquid water, μ_{liquid} , was made by relating it to the gas phase dipole moment, μ_{gas} , and the Kirkwood correlation parameter, g , as $\mu_{\text{liquid}} = g \times \mu_{\text{gas}}$. Using this, an estimate for the first hyperpolarizability was reported as $\bar{\beta} = 0.46 \times 10^{-31}$ esu = 5.3 a.u. in the **X** convention. Converting it to the **T** convention and correcting for the reference values, gives $\bar{\beta} = 5.3 \times 4 \times 0.30 / 0.335 = 19.1$ a.u. This value for the first hyperpolarizability of liquid water is considerably larger than the values obtained in this work, even if the damping of the DRF operator at short distances is ignored, but the sign change found experimentally is reproduced in the calculations. However, previous theoretical studies⁷⁵⁻⁷⁷ indicate that especially the first hyperpolarizability of water in the condensed phase is sensitive to the local environment. An indication of this is also seen in this work, since the first hyperpolarizability is much more sensitive to the damping of the DRF operator than the second hyperpolarizability. Therefore, it can be expected that especially the value for $\bar{\beta}$ will change if a more realistic local solvent environment is used in the calculations. Further investigation of the sensitivity of the first and second hyperpolarizability to changes in the local discrete environment has to be made before anything conclusive can be said.

V. CONCLUSIONS

In this work we presented a discrete solvent reaction field (DRF) model for the calculation of frequency-dependent hyperpolarizabilities of molecules in solution. The DRF model combines a density functional theory (DFT) description of the solute with a polarizable classical description of the discrete solvent molecules. The first hyperpolarizability is obtained in an efficient way within time-dependent DFT by using the $(2n+1)$ rule to reformulate the quadratic response equations into contributions known from a solution of the linear response equations. The method was tested for a water molecule embedded in a cluster of 127 classical water molecules. Frequency-dependent first and second hyperpolarizabilities related to the electric field induced second harmonic generation (EFISH) experiment were calculated both in the gas phase and in the liquid phase. For water in the gas phase, results in good agreement with high-level correlated wave function methods and experiments were obtained by using the so-called shape-corrected xc-potentials (SAOP and BP-GRAC). In the liquid phase the effect of using asymptotically correct functionals was discussed. It was shown that the first hyperpolarizability was more sensitive to damping of the interactions at short range than the second hyperpolarizability. The experimental change of sign for the first hyperpolarizability in going from gas to liquid was reproduced with the model.

ACKNOWLEDGMENTS

L.J. thanks Professor David P. Shelton for valuable comments on the conventions used in the liquid phase EFISH experiments for water. L.J. gratefully acknowledges The Danish Research Training Council for financial support.

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