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Cubic Optical Response of Molecules in a Nonequilibrium and Equilibrium Solvation Model

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The cubic response equations governing nonequilibrium and equilibrium solvation in the continuum approach are derived and implemented. We consider solvent effects on the frequency dependent second hyperpolarizability. We illustrate the effects of optical and static dielectric constants through sample calculations on H_2O and H_2CO.

I. Introduction

The technological interest for nonlinear optical (NLO) materials has generated a vast field of experimental and theoretical techniques over the last two decades and a fair amount of attention has been given to the quadratic optical response of matter. However, from a technical point of view, cubic optical response properties of matter are those of real applicability in future optical devices.[1−6]

Primarily, experimental efforts have focussed on measuring NLO effects in the condensed phase—solids, pure liquids, or molecules in solution—since most potentially interesting NLO systems decompose upon evaporation. Furthermore, the interest for the condensed phase stems from the practical realization of processable optical devices. From a theoretical standpoint reproducing condensed phase NLO measurements, using first principles methods, is extremely difficult. The inherent problem of optical processes in condesed systems is the coupling of processes on a wide range of time scales. In principle, it requires a conjunction of theories describing processes on the pico second scale down to instantaneous events. The latter, however are suitably described in the framework of electronic structure theory.

Ab initio electronic structure investigations for small molecules in vacuum, for which gas phase measurements exist, show that computation of NLO properties of isolated molecules are realizable but demanding. Furthermore, the response methodology[7] has proven successful in the computation of dynamic, electronic first hyperpolarizabilities (β),[8−11] and second hyperpolarizabilities (γ).[11,9,12−18]

The above motivates our on-going work with the multiconfigurational self-consistent reaction field (MCSCRF) solvation response model. Previously, it has been described and implemented for linear[19,20] and quadratic[21] optical response of molecules in equilibrium and nonequilibrium solvation.

Presently we focus on the extension of the response method to cubic response, leaving the basic solvation model unaltered. This enables, for the first time, correlated ab initio computations of the dynamic second hyperpolarizability within the dielectric, equilibrium, and nonequilibrium continuum solvent model.

Contrary to structural properties and ground state energies for a solvated molecule, the description of dynamic NLO molecular properties strongly depends on the manifold of excited states for the solute−solvent system. Previously, this has been considered using semiempirical methods,[22−25] RPA or time-dependent HF,[26] and MCSCF response theory.[19,27,20] In the case of dynamic second hyperpolarizabilities, only recently Cammi et al.[26] invoked the polarizable continuum model at the HF level to model solvation of molecules.

In the theory section we briefly reiterate our solvent model, the solvent response method, and show the derivation of the cubic solvent response equations. The implementation of these equations is illustrated with sample calculations of γ for H_2O and H_2CO in different solvents. In discussing these results, we address the effect of equilibrium and nonequilibrium solvation on γ and its dispersion.

The NLO properties of molecules are sensitive to the molecular environment,[23,28,29,30,27] especially for hydrogen bonded species such as H_2O[31,32] and H_2CO. Consequently, only qualitative trends for the second hyperpolarizability should be expected from such preliminary sample computations, as previously established for H_2O.[32]

The cubic optical response is the first NLO effect which does not average out in isotropic systems. In our present use of the continuum model we assume full isotropy of the solution. As mentioned above, from electronic structure computations only-electronic contributions to γ are accessable. Despite the fact that our method allows for the evaluation of the entire γ tensor for abitrary frequencies, here we exclusively address third harmonic generation (THG), $\gamma(-3\omega;\omega,\omega,\omega)$. For solute−solvent systems, one must expect this process being the least

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perturbed by nonelectronic degrees of freedoms, when considering optical frequencies.

II. Theory

A. Equilibrium and Nonequilibrium Solvent Models. The solvent model employed is a generalization of Kirkwood's original model,[33−35] where solvation is modeled by surrounding the solute with an isotropic and homogeneous dielectric medium. Among the many cavity shapes in use, we employ the simple spherical cavity, having only the cavity radius, R_{cav}, as a parameter. The solute molecule is placed with its center of mass at the origin of the cavity, and formally represented in terms of a multipole expansion (of order l,m) of its molecular charge distribution, $\rho(\mathbf{r},t)$. The dielectric medium is characterized by a linear and macroscopic electric polarization vector, $\mathbf{P}(t)$, with a correspondent dielectric constant, $\epsilon(t)$.

For the dielectric response to changes in $\rho(\mathbf{r},t)$, we use the approximation that solvent dynamics, on various time scales, may be partitioned into infinitly fast and slow processes. Thus, the total polarization vector $\mathbf{P}$ has only an optical and inertial contribution,

$$\mathbf{P} = \mathbf{P}_{\mathrm{op}} + \mathbf{P}_{\mathrm{in}} \tag{1}$$

with the dielectric medium characterized by the optical ϵ_{op} and static ϵ_{st} dielectric constants, respectively.

Prior to the application of high frequency, external radiation, the solute−solvent system is thought to be in internal equilibrium. This equilibrium configuration is defined by $\mathbf{P}_{\mathrm{in}}$, the choice of which in principle is arbitrary. The corresponding molecular electronic state is $|0\rangle$ and the molecular charge distribution ρ_{i}. Upon interaction with electromagnetic radiation, only $\mathbf{P}_{\mathrm{op}}$ may adjust to sudden changes in the molecular state ($|0\rangle \rightarrow |\tilde{0}\rangle$) which results in the new molecular charge distribution, ρ_{f}. However, $\mathbf{P}_{\mathrm{in}}$ remains unaltered reflecting the solute charge distribution prior to the electromagnetic perturbation. The result is a nonequilibrium solvent−solute configuration where the solvation energy is given by

$$E_{\mathrm{sol}}^{\mathrm{neq}} = \sum_{lm} g_l(\epsilon_{\mathrm{op}})\langle \mathrm{T}_{lm}(\rho_{\mathrm{f}})\rangle\langle \mathrm{T}_{lm}(\rho_{\mathrm{f}})\rangle + \sum_{lm} g_l(\epsilon_{\mathrm{st}}, \epsilon_{\mathrm{op}})[2\langle \mathrm{T}_{lm}(\rho_{\mathrm{f}})\rangle - \langle \mathrm{T}_{lm}(\rho_{\mathrm{i}})\rangle]\langle \mathrm{T}_{lm}(\rho_{\mathrm{i}})\rangle \tag{2}$$

The expectation values in eq 2 are obtained according to $\langle T_{lm}\rangle = T_{lm}^{\mathrm{n}} - \langle T^{\mathrm{e}}{}_{lm}\rangle$ and taken with respect to either $|0\rangle$ or $|\tilde{0}\rangle$. The nuclear charge moments are given as

$$T_{lm}^{\mathrm{n}} = \sum_g Z_g t^{\mathrm{lm}}(\mathbf{R}_g) \tag{3}$$

where Z_g is the charge of nucleus g and $\mathbf{R}_g$ its position. Similarly, the electronic charge moments are given as

$$T_{lm}^{\mathrm{e}} = \sum_{pq} t_{pq}^{lm} E_{pq} = \sum_{pq} \langle \phi_p | t^{lm}(\mathbf{r}) | \phi_q \rangle E_{pq} \tag{4}$$

with $t^{lm}(\mathbf{r})$ being the lmth component of the real spherical harmonics and ϕ_i the ith molecular orbital. E_{pq} is the second quantization spin-free operator

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^{\dagger} a_{q\sigma} \tag{5}$$

which annihilates an electron in φ_q (of spin symmetry σ) and creates it in φ_p. The reaction field factors, describing the response of the dielectric medium, are given as

$$g_l(\epsilon) = -\frac{R_{\mathrm{cav}}^{-(2l+1)}(l+1)(\epsilon-1)}{2[l+\epsilon(l+1)]} \tag{6}$$

and

$$g_l(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}}) = g_l(\epsilon_{\mathrm{st}}) - g_l(\epsilon_{\mathrm{op}}) \tag{7}$$

Applying a static external field does not give rise to a nonequilibrium configuration: changes in $\rho(\mathbf{r},t)$ occur infinitely slow such that all solvent degrees of freedom have time to equilibrate. In this limit, therefore, $\rho_i = \rho_f$ and eq 2 reduces to

$$E_{\mathrm{sol}}^{\mathrm{eq}} = \sum_{lm} g_l(\epsilon_{\mathrm{st}})|\langle \mathrm{T}_{\mathrm{lm}}(\rho_{\mathrm{f}})\rangle|^2 \tag{8}$$

which we refer to as equilibrium solvation.

In order to describe the time evolution of our model system we need a Hamiltonian of the form,

$$H(t) = H_o + \tilde{W}_{\mathrm{sol}} + V_{\mathrm{pert}}(t) \tag{9}$$

where (i) H_{o} is the nonrelativistic many-electron Hamiltonian for the molecule in vacuum, (ii) $\tilde{W}_{\mathrm{sol}}$ is the effective solvent-solute interaction operator, which depends on the current molecular state $|\tilde{0}\rangle$, and (iii) $V_{\mathrm{pert}}(t)$ is the operator for the interaction between the solute and the external frequency dependent electromagnetic radiation field. The effective solvent−solute interaction operator is written as

$$\tilde{W}_{\mathrm{sol}} = \sum_{lm} g_l(\epsilon_{\mathrm{op}})(T_{lm}^{\mathrm{n}})^2 + \sum_{lm} g(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}})(T_{lm}^{\mathrm{n}})^2 + \tilde{T}_g(\epsilon_{\mathrm{st}}, \epsilon_{\mathrm{op}}) \tag{10}$$

and is obtained using Frenkel's[36] variational principle for approximate wave functions: the solvent interaction operator must give similar time independent properties as obtained from derivatives of the energy expression. Therefore, it is not the operator that gives the solvent contribution to the total energy.[19,37,38] The interactions between the nuclear framework and the solvent give rise to the first two terms in eq 10 which involve optical and inertial polarization contributions. The third term we write as

$$\tilde{T}_g(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}}) = g_{\mathrm{sol}}^{(\mathrm{a})} + \tilde{g}_{\mathrm{sol}}^{(\mathrm{b})} + g_{\mathrm{sol}}^{(\mathrm{c})} \tag{11}$$

where

$$g_{\mathrm{sol}}^{(\mathrm{a})} = -2\sum_{lm} g_l(\epsilon_{\mathrm{op}}) T_{lm}^{\mathrm{e}}\, T_{lm}^{\mathrm{n}}$$

$$\tilde{g}_{\mathrm{sol}}^{(\mathrm{b})} = 2\sum_{lm} g_l(\epsilon_{\mathrm{op}}) T_{lm}^{\mathrm{e}} \langle \tilde{0} | T_{lm}^{\mathrm{e}} | \tilde{0} \rangle$$

$$g_{\mathrm{sol}}^{(\mathrm{c})} = -2\sum_{lm} g_l(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}}) \langle T_{lm}(\rho_i)\rangle T_{lm}^{\mathrm{e}} \tag{12}$$

In decending order the three terms in eq 12 represent (i) the optical polarization, induced by the electronic charge distribution, interacting with the solute's nuclear charge distribution, (ii) the interactions between the optical polarization, due to the electronic charge distribution, and the electronic charge of the solute, and (iii) the inertial polarization interacting with the electronic charge distribution.

Of the three terms we recognize that the instantaneous coupling between the optical polarization and the molecular electronic subsystem is due to $\tilde{g}_{\mathrm{sol}}^{(\mathrm{b})}$. Note, further, that the limit of equilibrium solvation can be obtained by setting $\epsilon_{\mathrm{op}} = \epsilon_{\mathrm{st}}$ such that $\tilde{T}_{\mathrm{g}}$ becomes

$$T^{g}(\epsilon) = g_{\mathrm{sol}}^{(\mathrm{a})} + g_{\mathrm{sol}}^{(\mathrm{b})} + g_{\mathrm{sol}}^{(\mathrm{c})} \tag{13}$$

as used in previous equilibrium studies.[19]

B. Response Method. The time evolution of the electromagnetically perturbed solvent−solute system is propagated using Ehrenfest's equations of motion

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\tilde{0}|\mathbf{T}^{\dagger}|\tilde{0}\rangle = \left\langle\tilde{0}\left|\frac{\mathrm{d}}{\mathrm{d}t}\tilde{\mathbf{T}}^{\dagger}\right|\tilde{0}\right\rangle - i\langle\tilde{0}|[\tilde{\mathbf{T}}^{\dagger},H]|\tilde{0}\rangle \tag{14}$$

for a set of operators

$$\mathbf{T} = (\mathbf{q}^{\dagger},\mathbf{R}^{\dagger},\mathbf{q},\mathbf{R}) \tag{15}$$

defined according to

$$R_n^{\dagger} = |n\rangle\langle 0|$$

$$q_k^{\dagger} = E_{pq}, \quad p > q \tag{16}$$

In eq 16, $R_n^{\dagger}$ are the state transfer operators responsible for mixing of the reference state, $|0\rangle$, with states in the orthogonal complement $\{|n\rangle\}$, whereas $q_k^{\dagger}$ induces mixing among orbitals. Using these operators we define Hermitian generators of unitary transformations in configuration space

$$S(t) = \sum_{n}(S_n(t)R_n^{\dagger} + S_n^{*}(t)R_n) \tag{17}$$

and orbital space

$$\begin{aligned}\kappa(t) &= \sum_{rs}(\kappa_{rs}(t)E_{rs} + \kappa_{rs}^{*}(t)E_{sr}) \\ &= \sum_{k}(\kappa_k(t)q_k^{\dagger} + \kappa_k^{*}(t)q_k)\end{aligned} \tag{18}$$

the time dependent amplitudes of which are collected in a vector

$$\beta = \begin{pmatrix}\boldsymbol{\kappa} \\ \mathbf{S} \\ \boldsymbol{\kappa}^{*} \\ \mathbf{S}^{*}\end{pmatrix} \tag{19}$$

Since we consider time-dependent perturbations, the amplitudes must be expressed in a more general basis $\{\mathbf{O}\}$ (ref 7) such that

$$\kappa(t) + S(t) = \mathbf{T}\boldsymbol{\beta} = \mathbf{O}\,\boldsymbol{\alpha} \tag{20}$$

This operator basis is split into a configuration and an orbital part according to

$$O_j = O_{\mathrm{o}j} + O_{\mathrm{c}j} \tag{21}$$

which allows the amplitudes to be written separately as

$$\kappa(t) = \sum_{j}\alpha_j(t)O_{\mathrm{o}j}$$

$$S(t) = \sum_{j}\alpha_j(t)O_{\mathrm{c}j} \tag{22}$$

The unitary transformations in configuration and orbital space are obtained using the operators: $\mathrm{e}^{iS(t)}$ and $\mathrm{e}^{i\kappa(t)}$. Taking our reference state $|0\rangle$ as an MCSCF state, the evolution of the molecular state is parametrized as

$$|\tilde{0}\rangle = \mathrm{e}^{i\kappa(t)}\mathrm{e}^{iS(t)}|0\rangle \tag{23}$$

Further, the time-transformed elementary operators occuring in eq 14 are given as

$$\tilde{q}_{pq}^{\dagger} = \mathrm{e}^{i\kappa(t)}q_{pq}^{\dagger}\mathrm{e}^{-i\kappa(t)}$$

$$\tilde{q}_{pq} = \mathrm{e}^{i\kappa(t)}q_{pq}\mathrm{e}^{-i\kappa(t)}$$

$$\tilde{R}_n^{\dagger} = \mathrm{e}^{i\kappa(t)}\mathrm{e}^{iS(t)}R_n^{\dagger}\mathrm{e}^{-i\kappa(t)}\mathrm{e}^{-iS(t)}$$

$$\tilde{R}_n = \mathrm{e}^{i\kappa(t)}\mathrm{e}^{iS(t)}R_n\mathrm{e}^{-i\kappa(t)}\mathrm{e}^{-iS(t)} \tag{24}$$

The Hamiltonian used in eq 14 we take from eq 9, and for the solvent−solute interaction, $\tilde{W}_{\mathrm{sol}}$ we note that only $\tilde{T}_g(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}})$ contributes to the Ehrenfest equation. It is convenient to rewrite the solvent−solute interaction operator as:

$$\tilde{W} = \{g_{\mathrm{sol}}^{(\mathrm{a})} + g_{\mathrm{sol}}^{(\mathrm{c})}\} + \tilde{g}_{\mathrm{sol}}^{(\mathrm{b})} = g_{\mathrm{sol}}^{(\mathrm{a+c})} + \sum_{lm}C^{lm}\langle\tilde{0}|D^{lm}|\tilde{0}\rangle \tag{25}$$

where $C^{lm} = 2g_l(\epsilon_{\mathrm{op}})T_{lm}^{\mathrm{e}}$ and $D^{lm} = T_{lm}^{\mathrm{e}}$. Thus, at this point we write eq 14 as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\tilde{0}|\tilde{\mathbf{O}}^{\dagger}|\tilde{0}\rangle = \left\langle\tilde{0}\left|\frac{\mathrm{d}}{\mathrm{d}t}\tilde{\mathbf{O}}^{\dagger}\right|\tilde{0}\right\rangle - i\langle\tilde{0}|[\tilde{\mathbf{O}}^{\dagger},H_0 + V(t)]|\tilde{0}\rangle - \\ i\langle\tilde{0}|[\tilde{\mathbf{O}}^{\dagger},g_{sol}^{(a+c)}]|\tilde{0}\rangle - i\sum_{lm}\langle\tilde{0}|[\tilde{\mathbf{O}}^{\dagger},C^{lm}]|\tilde{0}\rangle\langle\tilde{0}|D^{lm}|\tilde{0}\rangle\end{aligned} \tag{26}$$

Previously, Olsen et al.[7] derived the matrix representation of eq 14 for the situation where the molecule is in vacuum. Our concern, therefore, are contributions from the last two terms in eq 26, which principally have the following structure

$$\langle\tilde{0}|[\tilde{\mathbf{O}}^{\dagger},C\langle\tilde{0}|D|\tilde{0}\rangle]|\tilde{0}\rangle = \langle\tilde{0}|[\tilde{\mathbf{O}}^{\dagger},C]|\tilde{0}\rangle\langle\tilde{0}|D|\tilde{0}\rangle \tag{27}$$

with C and D being time-independent operators. Following the procedure from ref 7, we obtain the following matrix representation of eq 14

$$\begin{aligned}\sum_{n=1}^{\infty}(\mathrm{i})^{n}S_{j,h_1,h_2,\ldots h_n}^{[n+1]}\dot{\alpha}_{\mathrm{h}_1}(t)\prod_{\mu=2}^{n}\alpha_{h_\mu}(t) = -\sum_{n=0}^{\infty}(i)^{n+1}\{E_{j,h_1,h_2,\ldots,h_n}^{[n+1]} + \\ V_{j,h_1,h_2,\ldots h_n}^{t[n+1]}\}\prod_{\mu=1}^{n}\alpha_{h_\mu}(t) - \sum_{n=0}^{\infty}(i)^{n+1}\{G_{j,h_1,h_2,\ldots,h_n}^{[n+1]} + \\ \sum_{k=0}^{n}\sum_{lm}C_{j,h_{(1+k)},\ldots,h_n}^{lm[n-k+1]}\,D_{h_1,h_2,\ldots,h_k}^{lm[k]}\}\prod_{\mu=1}^{n}\alpha_{h_\mu}(t)\end{aligned} \tag{28}$$

where the definitions of $S_{j,h_1,h_2,\ldots,h_n}^{[n+1]}$, $E_{j,h_1,h_2,\ldots,h_n}^{[n+1]}$, and

$V^{t[n+1]}_{j,h_1,h_2,...,h_n}$ are given in ref 7. The remaining terms are

$$D^{lm[n]}_{h_1h_2...h_n} = \sum_{k=0}^{n} \frac{(-1)^n}{k!(n-k)!} \langle 0| \prod_{\mu=1}^{k} \hat{O}_{ch_\mu} \prod_{\mu=k+1}^{n} \tilde{O}_{oh_\mu} D^{lm}|0\rangle \qquad (29)$$

and

$$X^{[n+1]}_{j,h_1,h_2,...h_n} = \sum_{k=0}^{n} \frac{(-1)^n}{k!(n-k)!} (\langle 0|[O^\dagger_{cj}, \prod_{\mu=1}^{k} \hat{O}_{ch_\mu} \prod_{\mu=k+1}^{n} \hat{O}_{oh_\mu} X]|0\rangle + \langle 0| \prod_{\mu=1}^{k} \hat{O}_{ch_\mu} [O^\dagger{}_{oj}, \prod_{\mu=k+1}^{n} \hat{O}_{oh_\mu} X]|0\rangle) \qquad (30)$$

where commutation is represented by the following superoperator notation: $\hat{A}(B) = [A, B]$. The matrix components, $E^{[n+1]}_{j,h_1,h_2,...,h_n}$, $G^{[n+1]}_{j,h_1,h_2,...,h_n}$, and $C^{lm[n+1]}_{j,h_1,h_2,...,h_n}$ are given by the following substitutions:

$$X = H_0 \quad \rightarrow \quad E^{[n+1]}_{j,h_1,h_2,...,h_n}$$

$$X = g^{(a+c)}_{sol} \quad \rightarrow \quad G^{[n+1]}_{j,h_1,h_2,...,h_n}$$

$$X = C^{lm} \quad \rightarrow \quad C^{lm[n+1]}_{j,h_1,h_2,...,h_n} \qquad (31)$$

Until this point, no assumption on our reference state $|0\rangle$ was made since $\mathbf{P}_{in}$ could be chosen randomly. However, the electromagnetic interation operator has the form

$$V(t) = \int_{-\infty}^{\infty} d\omega V^{\omega} \exp[(-i\omega + \eta)t] \qquad (32)$$

where V^ω is the Fourier transform of $V(t)$ and η an infinitesimal positive number. Thus the perturbation is applied adiabatically, that is $V(t \rightarrow -\infty) = 0$, in which case $W_{sol}(t \rightarrow -\infty) = W_{sol}$. As a natural choice, we optimize the reference state subject to the generalized Brillouin condition, allowing full relaxation of P_{in},

$$\begin{pmatrix} \langle 0|[\mathbf{q}^\dagger, H_o + W]|0\rangle \\ \langle 0|[\mathbf{R}^\dagger, H_o + W]|0\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad (33)$$

where

$$W = g^{a+c}_{sol} + \sum_{lm} C^{lm}\langle 0|D^{lm}|0\rangle \qquad (34)$$

C. Implementation of the Solvent Contributions to the Cubic Response Equations. The implementation of the cubic response equations with nonequilibrium or equilibrium solvent configurations is based on previous program developments within the DALTON program.[7,19−21,27,39−42] From a practical point of view, we utilize that the vacuum part of eq 28 already has been implemented for linear,[7] quadratic,[40] and cubic[41] response theory. We obtain the cubic solvent response by adding the third order solvent contribution to the corresponding vacuum equations. The third-order solvent contributions in eq 28 we write as

$$O^3(-i\langle\tilde{0}|[\tilde{\mathbf{O}}^\dagger, \tilde{W}]|\tilde{0}\rangle) = iG^{[4]}_{j,h_1h_2h_3}\alpha_{h_1}\alpha_{h_2}\alpha_{h_3} + i\sum_{lm}\{D^{lm[3]}_{h_1h_2h_3}\, C^{lm[1]}_{j} + D^{lm[2]}_{h_1h_2}\, C^{lm[2]}_{j,h_3} + D^{lm[1]}_{h_1}\, C^{lm[3]}_{j,h_2h_3} + D^{lm[0]}C^{lm[4]}_{j,h_1h_2h_3}\}\alpha_{h_1}\alpha_{h_2}\alpha_{h_3} \qquad (35)$$

The evaluation of the terms from $C^{lm[n+1]}_{j,h_1,h_2,...,h_n}$ and $D^{lm[n]}_{h_1h_2...,h_n}$ through third order is presented in Appendix A.

It is advantageous to define the following effective solvent operators:

$$A = \sum_{lm} C^{lm}\langle 0|D^{lm}|0\rangle = 2\sum_{lm} g_l(\epsilon_{op})\langle 0|T^e_{lm}|0\rangle T^e_{lm} \qquad (36)$$

$$W = A + g^{(a+c)}_{sol} = A - 2\sum_{lm}\{g_l(\epsilon_{op})T^n_{lm} + g_l(\epsilon_{st},\epsilon_{op})\langle T(\rho_i)\rangle\}T^e_{lm} \qquad (37)$$

$$A^1 = 2\sum_{lm} g_l(\epsilon_{op})\{\langle 0|T^e_{lm}(^1\kappa)|0\rangle + \langle 0^{1L}|T^e_{lm}|0\rangle + \langle 0|T^e_{lm}|0^{1R}\rangle\}T^e_{lm} \qquad (38)$$

$$B^1 = -\frac{2}{3}\sum_{lm} g_l(\epsilon_{op})\{\langle 0|T^e_{lm}|0^{1R}\rangle + \langle 0^{1L}|T^e_{lm}|0\rangle|\}T^e_{lm} \qquad (39)$$

$$A^{12} = \sum_{lm} g_l(\epsilon_{op})(\langle 0|T^e_{lm}(^1\kappa,{}^2\kappa)|0\rangle + 2(\langle 0^{1L}|T^e_{lm}(^2\kappa)|0\rangle + \langle 0|T^e_{lm}(^2\kappa)|0^{1R}\rangle) + (\langle 0^{1L}|T^e_{lm}|0^{2R}\rangle + \langle 0^{2L}|T^e_{lm}|0^{1R}\rangle))T^e_{lm} \qquad (40)$$

$$A^{123} = \sum_{lm} g_l(\epsilon_{op})(\frac{1}{3}\langle 0|T^e_{lm}(^1\kappa,{}^2\kappa,{}^3\kappa)|0\rangle + (\langle 0^{1L}|T^e_{lm}(^2\kappa,{}^3\kappa)|0\rangle + \langle 0|T^e_{lm}(^2\kappa,{}^3\kappa)|0^{1R}\rangle) + (\langle 0^{1L}|T^e_{lm}(^3\kappa)|0^{2R}\rangle + \langle 0^{2L}|T^e_{lm}(^3\kappa)|0^{1R}\rangle))T^e_{lm} \qquad (41)$$

In eqs 38−41 and the following we use transformed states defined as

$$|0^R\rangle = -\sum_n S_n|n\rangle \qquad (42)$$

$$\langle 0^L| = \sum_n S^*_n\langle n| \qquad (43)$$

along with index transformation of solvent integrals defined as

$$Y(^1\kappa) = [^1\kappa(t), Y]$$

$$Y(^1\kappa,{}^2\kappa) = [^2\kappa(t),[^1\kappa(t), Y]]$$

$$Y(^1\kappa,{}^2\kappa,{}^3\kappa) = [^3\kappa(t),[^2\kappa(t),[^1\kappa(t), Y]]] \qquad (44)$$

We obtain, using the above solvent effective operators, the following solvent contributions to $E^{[4]}N^1N^2N^3$ in cubic response:

$$
\begin{aligned}
-W^{[4]}_{j(klm)}\,N^1_k\,N^2_l\,N^3_m = P(1,2,3)\Bigg\{&\left(\frac{1}{2}\langle 0^{2L}|W|0^{3R}\rangle + \frac{2}{3}\Big\langle 0\Big|W+\frac{3}{2}A\Big|0\Big\rangle^2 S_n\,{}^3S'_n\right)\begin{pmatrix} O \\ {}^1S_j \\ 0 \\ {}^1S'_j \end{pmatrix} + \\
&{}^2S_n\,{}^3S'_n\begin{pmatrix} \frac{2}{3}\left(\Big\langle 0^{1L}\Big|\Big[q_j, W+\frac{3}{2}A\Big]\Big|0\Big\rangle + \Big\langle 0\Big|\Big[q_j, W+\frac{3}{2}A\Big]\Big|0^{1R}\Big\rangle\right) \\ \frac{1}{6}\Big\langle j\Big|W+\frac{3}{2}A\Big|0^{1R}\Big\rangle \\ \frac{2}{3}\left(\Big\langle 0^{1L}\Big|\Big[q_j^\dagger, W+\frac{3}{2}A\Big]\Big|0\Big\rangle + \Big\langle 0\Big|\Big[q_j^\dagger, W+\frac{3}{2}A\Big]\Big|0^{1R}\Big\rangle\right) \\ -\frac{1}{6}\Big\langle 0^{1L}\Big|W+\frac{3}{2}A\Big|j\Big\rangle \end{pmatrix} + \frac{1}{2}\begin{pmatrix} \langle 0^{1L}|[q_j, W({}^3\kappa)+A^3]|0^{2R}\rangle + \langle 0^{2L}|[q_j, W({}^3\kappa)+A^3]|0^{1R}\rangle \\ 0 \\ \langle 0^{1L}|[q_j^\dagger, W({}^3\kappa)+A^3]|0^{2R}\rangle + \langle 0^{2L}|[q_j^\dagger, W({}^3\kappa)+A^3]|0^{1R}\rangle \\ 0 \end{pmatrix} + \\
&\begin{pmatrix} 0 \\ \left(\frac{1}{2}\langle 0^{2L}|W({}^3\kappa)+A^3|0\rangle + \langle 0|W({}^3\kappa)+A^3|0^{2R}\rangle\right){}^1S_j \\ 0 \\ \left(\langle 0^{2L}|W({}^3\kappa)+A^3|0\rangle + \frac{1}{2}\langle 0|W({}^3\kappa)+A^3|0^{2R}\rangle\right){}^1S'_j \end{pmatrix} + {}^1S_n\,{}^2S'_n\begin{pmatrix} \langle 0|[q_j, W({}^3\kappa)+A({}^3\kappa)+2\mathrm{A}^3+B^3]|0\rangle \\ \frac{1}{2}\langle j|W({}^3\kappa)+A({}^3\kappa)+2A^3+B^3|0\rangle \\ \langle 0|[q_j^\dagger, W({}^3\kappa)+A({}^3\kappa)+2A^3+B^3]|0\rangle \\ -\frac{1}{2}\langle 0|W({}^3\kappa)+A({}^3\kappa)+2\mathrm{A}^3+B^3|j\rangle \end{pmatrix} + \\
&\frac{1}{2}\begin{pmatrix} \langle 0^{1L}|[q_j, W({}^2\kappa,{}^3\kappa)+2A^{23}+2A^2({}^3\kappa)]|0\rangle + \langle 0|[q_j, W({}^2\kappa,{}^3\kappa)+2A^{23}+2A^2({}^3\kappa)]|0^{1R}\rangle \\ \langle j|W({}^2\kappa, {}^3\kappa)+2A^{23}+2A^2({}^3\kappa)|0^{1R}\rangle \\ \langle 0^{1L}|[q_j^\dagger, W({}^2\kappa,{}^3\kappa)+2A^{23}+2A^2({}^3\kappa)]|0\rangle + \langle 0|[q_j^\dagger, W({}^2\kappa,{}^3\kappa)+2A^{23}+2A^2({}^3\kappa)]|0^{1R}\rangle \\ -\langle 0^{1L}|W({}^2\kappa, {}^3\kappa)+2A^{23}+2A^2({}^3\kappa)|j\rangle \end{pmatrix} + \\
&\frac{1}{2}\langle 0|W({}^2\kappa,{}^3\kappa)+2A^{23}+2A^2({}^3\kappa)|0\rangle\begin{pmatrix} 0 \\ {}^1S_j \\ 0 \\ {}^1S'_j \end{pmatrix} + \frac{1}{6}\begin{pmatrix} \langle 0|[q_j, W({}^1\kappa,{}^2\kappa,{}^3\kappa)+6A^{123}+6A^{12}({}^3\kappa)+3A^1({}^2\kappa,{}^3\kappa)]|0\rangle \\ \langle j|W({}^1\kappa,{}^2\kappa,{}^3\kappa)+6A^{123}+6A^{12}({}^3\kappa)+3A^1({}^2\kappa,{}^3\kappa)|0\rangle \\ \langle 0|[q_j^\dagger, W({}^1\kappa,{}^2\kappa,{}^3\kappa)+6A^{123}+6A^{12}({}^3\kappa)+3A^1({}^2\kappa,{}^3\kappa)]|0\rangle \\ -\langle 0|W({}^1\kappa,{}^2\kappa,{}^3\kappa)+6A^{123}+6A^{12}({}^3\kappa)+3A^1({}^2\kappa,{}^3\kappa)|j\rangle \end{pmatrix} + \\
&\frac{3}{4}\,{}^2S_n\,{}^3S'_n\begin{pmatrix} 0 \\ \langle j|A|0^{1R}\rangle \\ 0 \\ -\langle 0^{1L}|A|j\rangle \end{pmatrix} + \frac{1}{2}\,{}^2S_n\,{}^3S'_n\begin{pmatrix} 0 \\ \langle j|A({}^3\kappa)+A^3+B^3|0\rangle \\ 0 \\ -\langle 0|A({}^3\kappa)+A^3+B^3|j\rangle \end{pmatrix}\Bigg\}
\end{aligned}
\tag{45}
$$

where $P(1,2,3)$ is the permutation operator. The above equations have the same structure as the corresponding response equations for the molecule in vacuum.[41] Therefore, the iterative algorithms for solving the sets of response equations or response eigenvalue equations that was introduced in refs 7, 40, and 41 are maintained. These algorithms involve linear transformations of the matrices with a trial vector.

III. Sample Calculations

As an illustration of the cubic response method for equilibrium and nonequilibrium solvent configurations we consider two solutes: H_2O and H_2CO. The electronic structure of the solutes are evaluated using a complete active space (CAS) wave function. The choice of active space was based on MP2 occupations numbers and having one correlating orbital for each strongly occupied orbital. The molecules are placed in the yz-plane such that molecular dipole moments point in the z direction. All computations were performed in the C_{2v} point group.

The geometry of H_2O is: $R_{OH} = 0.959$ Å and $\theta_{HOH} = 104.654°$, and the cavity radius is 2.37 Å, as used previously.[19−21] The formal multipole expansion of the molecular charge distribution was truncated after $l = 7$, which has been shown to give a proper description for H_2O.[35] Eight active electrons were distributed in the eight active orbitals $4a_1$, $2b_1$, and $2b_2$, and the core orbital of a_1 symmetry was kept inactive. The basis set employed was the ANO set designed by Widmark et al.[44] with a [13s8p6d/5s4p3d] contraction on oxygen and a [8s4p/4s3p] on hydrogen. For the vacuum molecule this gives a Hartree−Fock energy of −76.064960 au. In order to compare our present results with previous equilibrium and nonequilibrium, linear and quadratic solvent response properties, the choices of ϵ_{op} and ϵ_{st} are as in refs 20 and 21: (i) nonequilibrium

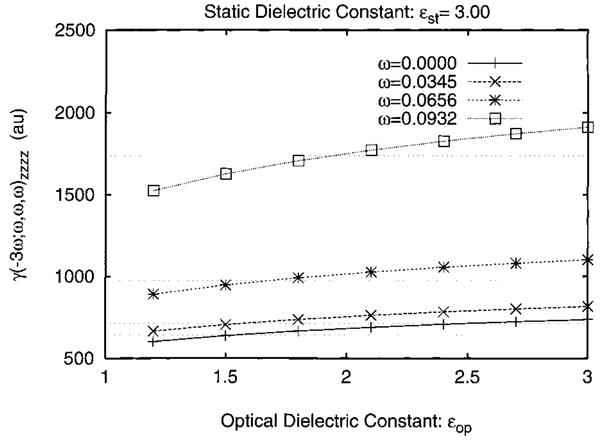

Figure 1. Nonequilibrium solvent calculations of $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$ of a solvated water molecule as a function of ϵ_{op} and with $\epsilon_{st} = 3.00$. The electronic wave function is a CAS wave function. The corresponding gas phase values are indicated with dotted lines.

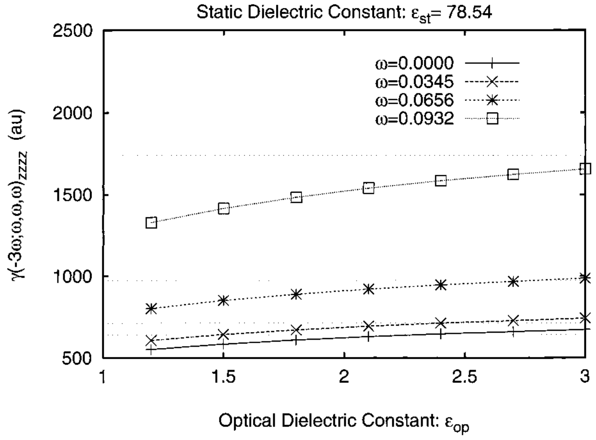

Figure 2. Nonequilibrium solvent calculations of $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$ of solvated water molecule as a function of ϵ_{op} and with $\epsilon_{st} = 78.54$. The electronic wave function is a CAS wave function. The corresponding gas phase values are indicated with dotted lines.

solvent configurations, variation of ϵ_{op} from 1.30 to 3.00 in steps of 0.3 while keeping ϵ_{st} equal to either 3.00 or 78.54; (ii) nonequilibrium solvent configurations, variation of ϵ_{st} from 3.00 to 78.54, keeping ϵ_{op} fixed at 1.80; and (iii) equilibrium solvent configurations, and ϵ_{st} is varied from 3.00−78.54.

For H_2CO we used a spherical cavity with a radius of 2.645 Å. The molecular geometry of H_2CO is from Herzberg,[45] and the multipole expansion taken to order l= 10. The complete active space is $6a_1$, $4b_2$, $2b_1$, and $0a_2$ with 12 active electrons, and we have used the basis set presented in ref 46. For the gas phase molecule we obtain the Hartree−Fock energy to be −113.503616 au. The choice of ϵ_{op} and ϵ_{st} corresponds to the following solvents: benzene ($\epsilon_{st} = 2.284$, $\epsilon_{op} = 2.244$), ethyl ether ($\epsilon_{st} = 4.335$, $\epsilon_{op} = 1.828$), 1-hexanol ($\epsilon_{st} = 13.3$, $\epsilon_{op} = 2.005$), acetone ($\epsilon_{st} = 20.7$, $\epsilon_{op} = 1.841$), methanol ($\epsilon_{st} = 32.63$, $\epsilon_{op} = 1.758$) and water ($\epsilon_{st} = 78.54$, $\epsilon_{op} = 1.778$).

IV. Results and Discussion

In the following we present computational results as obtained for H_2O and H_2CO for the second hyperpolarizability tensor. For sake of brevity, we present only the THG component along the dipole direction, that is, $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$, which we from now on simply refer to as γ.

A. H_2O. In Figures 1−4 we present CAS computations of γ at four different input frequencies: 0.0, 0.0345, 0.0656, and 0.0932 au. The corresponding gas phase values of γ are given as the dotted lines in these figures. Figure 1 and 2 display similar trends among which the strong dependence of different nonequilibrium solvent configurations is quite clear. For fixed ϵ_{st}, an increase in ϵ_{op} (which enhances the optical polarization contribution) is accompanied by an increase of the THG response. Also, for the individual frequencies γ originates below the corresponding gas phase value for small values of ϵ_{op}. For all but the case where $\epsilon_{st} = 78.54$ and $\omega = 0.0932$ au, we observe that the effects of nonequilibrium solvation lead to values of γ that supersed the gas phase value with increasing value of ϵ_{op}. The differences between Figure 1 and 2 primarily amount to the fact that, for given ϵ_{op}, the value of γ is attenuated due to shifting ϵ_{st} from 3.00 to 78.54. Furthermore, in Figure 1 we illustrate the limit where nonequilibrium solvation becomes equilibrium solvation: we see that γ increases with ϵ_{op} up to the point where $\epsilon_{op} = \epsilon_{st}$. Figure 3 clearly illustrates how the THG process (in the dipole direction) is impeded by increasing the inertial polarization for the nonequilibrium solvent configuration. The specific choice of ϵ_{op} corresponds to a value typical of common solvents. For small values of ϵ_{st}, at first the attenuation of γ is drastic, then the values of γ gradually level out at values below the corresponding gas phase values. Generally, these decreases are more pronounced as the frequency of the perturbing field increases. The situation in Figure 3 should be contrasted with Figure 4, where the effect on γ for equilibrium solvation is displayed for increasing ϵ. In this case the notion of inertial polarization is absent and starting from the gas phase value, γ is increased almost in an opposite manner as in Figure 3. Evidently, equilibrium and nonequilibrium solvation give rise to quite different behavior of the THG response at the CAS level of electron structure theory. For nonequilibrium solvation, qualitatively speaking, trends are similar at the Hartree−Fock level as we may confirm by comparing Figures 3 and 5. Primarily, electron correlation gives rise to larger values of γ, as also seen for the gas phase values.

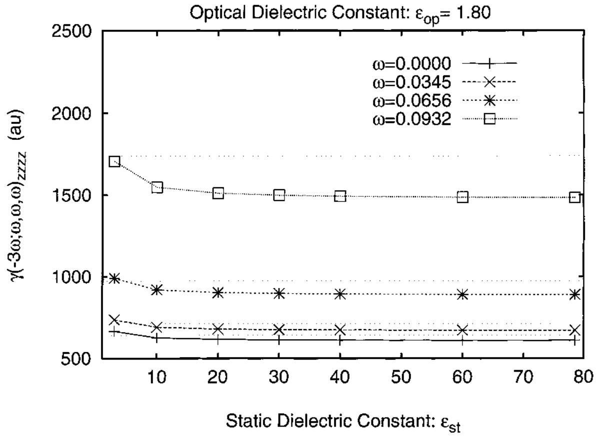

Figure 3. Nonequilibrium solvent calculations of $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$ of a solvated water molecule as a function of ϵ_{st} and with $\epsilon_{op} = 1.8$. The electronic wave function is a CAS wave function. The corresponding gas phase values are indicated with dotted lines.

The main conclusion for H_2O is that the dynamic THG response in the dipole direction increases for equilibrium and decreases for nonequilibrium solvation, relative to the gas phase values. This we understand in terms of the increase in γ for either situation: increasing the optical polarization contribution, that is, ϵ_{op}, while keeping ϵ_{st} constant, or decreasing the inertial polarization contribution, that is, ϵ_{st}, for a given ϵ_{op}. In either case the solvent configuration is allowed a larger flexibility to relax to changes in ρ during the interaction with the electro-

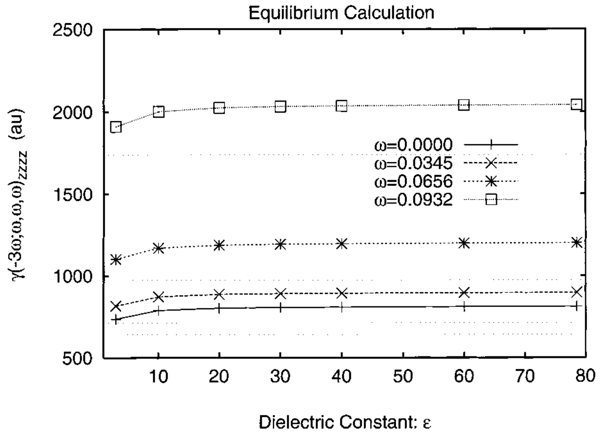

Figure 4. Equilibrium solvent calculations of $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$ of a solvated water molecule as a function of the dielectric constant. The electronic wave function is a CAS wave function. The corresponding gas phase values are indicated with dotted lines.

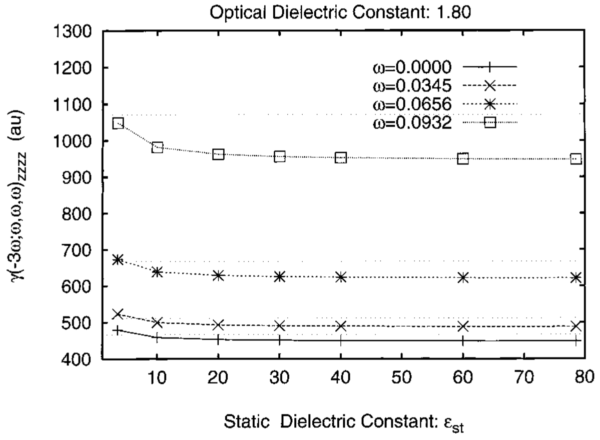

Figure 5. Nonequilibrium solvent calculations of $\gamma(-3\omega;\omega;\omega;\omega)_{zzzz}$ of a solvated water molecule as a function of ϵ_{st} and with $\epsilon_{op} = 1.8$. The electronic wave function is a SCF wave function. The corresponding gas phase values are indicated with dotted lines.

magnetic radiation field. Since equilibrium solvation represents the extreme of this picture (the entire polarization field may relax) then γ must be overestimated. With the spectral representation of γ in mind, the increases are also evident from the point of view of excitation energies. Assuming unaffected transition moments, an increase in the optical polarization leads to decreased excitation energies, and consequently increases in γ.

From this and our previous studies[19−21] it is clear that there is a tremendous difference between the results obtained in the equilibrium solvent model and the ones from the nonequilibrium solvent model. It is also clear that for high frequency external fields it is necessary to utilize the nonequilibrium solvent model.

B. H_2CO. In Table 1 we present the static and frequency dependent second hyperpolarizability γ of H_2CO for the equilibrium solvent model. The values of γ are the averaged second hyperpolarizability tensor elements parallel to the applied field. The solvents are benzene, ethyl ether, 1-hexanol, acetone, methanol, and water. Application of the equilibrium solvent model gives second hyperpolarizabilities that increase with increasing static dielectric constant, and for all solvents the value of γ increases compared to vacuum.

Utilization of the nonequilibrium solvent model gives rise to a completely different picture of the solvent dependence of the second hyperpolarizability. The averaged second hyperpolarizability decreases with increasing solvent polarity, and we observe a similar interplay between the optical and inertial polarizations as in refs 20 and 42. As the optical dielectric constant increases and thereby the optical polarization vector, the optical polarization of solvent increases. Within the nonequilibrium solvent model this increase leads to a better solvation of the solute. Comparatively, the values of γ in benzene and 1-hexanol are larger than expected from their values of the static dielectric constants.

TABLE 1: MCSCRF Response Calculations of State and Frequency Dependent Second Hyperpolarizabilities Using the Equilibrium Solvent Model[a]

vacuum or solvent	$\omega = 0.0$ (au)	$\omega = 0.0049$ (au)	$\omega = 0.0278$ (au)
vacuum	2368.86	2375.70	2606.80
benzene	3423.87	3433.68	3764.38
ethyl ether	4135.06	4146.88	4544.60
1-hexanol	4899.14	4913.13	5383.73
acetone	5059.77	5074.22	5560.34
methanol	5170.92	5185.69	5682.59
water	5288.50	5303.61	5811.97

[a] The presented numbers are the averaged second hyperpolarizabilities parallel to the applied field. The frequency of the field is denoted by ω. The units are au.

TABLE 2: MCSCRF Response Calculations of Static and Frequency Dependent Second hyperpolarizabilities Using the Nonequilibrium Solvent Model[a]

vacuum or solvent	$\omega = 0.0$ (au)	$\omega = 0.0049$ (au)	$\omega = 0.0278$ (au)
vacuum	2368.86	2375.70	2606.80
benzene	3394.83	3404.55	3731.97
ethyl ether	2902.36	2910.22	3174.20
1-hexanol	2904.09	2911.80	3170.36
acetone	2771.14	2778.43	3022.82
methanol	2700.79	2707.85	2944.45
water	2699.12	2706.19	2942.99

[a] The presented numbers are the averaged second hyperpolarizabilities parallel to the applied field. The frequency of the field is denoted by ω. The units are au.

The values of γ when H_2CO is solvated are for all solvents larger than the one where H_2CO is vacuum.

V. Perspective

We have presented the first method for treating fourth-order molecular properties of solvated molecules described by correlated electronic wave functions. We describe the solvent as a dielectric medium and its interactions with the solute as being between the optical and inertial polarization vectors and the solvated molecular charge distribution. The optical polarization is in equilibrium with the charge distribution of the solute. On the other hand, the inertial polarization vector is either in an equilibrium or a nonequilibrium state with respect to the solute charge distribution. The state of the inertial and optical polarization vector depends on the time-dependence of the external perturbation. We have presented the necessary mathematical derivations for the development of this method. Furthermore, we have implemented the cubic solvent response method in the DALTON program and presented sample calculations on H_2O and H_2CO.

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VI. Appendix A

Expansion of eq 30 to third order and introduction of the operators $\mathbf{T} = (\mathbf{q}, \mathbf{R}, \mathbf{q}^\dagger, \mathbf{R}^\dagger)$ gives

$$X_j^{[1]}[R_j^\dagger] = -\langle 0|X|j\rangle \tag{46}$$

$$X_j^{[1]}[R_j] = \langle j|X|0\rangle \tag{47}$$

$$X_j^{[1]}[q_j] = \langle 0|[q_j,X]|0\rangle \tag{48}$$

$$X_{j,l_1}^{[2]}[R_j^\dagger]\alpha_{l_1} = \langle 0|X(^1\kappa)|j\rangle - \langle 0|X|0\rangle{}^1S_j^* + \langle 0^{1L}|X|j\rangle \tag{49}$$

$$X_{j,l_1}^{[2]}[R_j]\alpha_{l_1} = -\langle j|X(^1\kappa)|0\rangle - \langle 0|X|0\rangle{}^1S_j - \langle j|X|0^{1R}\rangle \tag{50}$$

$$\begin{aligned} X_{j,l_1}^{[2]}[q_j]\alpha_{l_1} = -\langle 0|[q_j,X(^1\kappa)]|0\rangle - \langle 0|[q_j,X]|0^{1R}\rangle - \\ \langle 0^{1L}|[q_j,X]|0\rangle \end{aligned} \tag{51}$$

$$\begin{aligned} X_{j,l_1l_2}^{[3]}[R_j^\dagger]\alpha_{l_1}\alpha_{l_2} = -\frac{1}{2}\langle 0|X(^1\kappa,{}^2\kappa)|j\rangle - \langle 0^{1L}|X(^2\kappa)|j\rangle + \\ \frac{1}{2}(\langle 0|X|0^{2R}\rangle + \langle 0^{2L}|X|0\rangle + 2\langle 0|X(^2\kappa)|0\rangle)S_j^{1*} + \\ \frac{1}{2}\langle 0^{1L}|X|0\rangle S_j^{2*} - \frac{1}{2}\sum_n S_n^{1*}\,{}^2S_n\langle 0|X|j\rangle \end{aligned} \tag{52}$$

$$\begin{aligned} X_{j,l_1l_2}^{[3]}[R_j]\alpha_{l_1}\alpha_{l_2} = \frac{1}{2}\langle j|X(^1\kappa,{}^2\kappa)|0\rangle + \langle j|X(^2\kappa)|0^{1R}\rangle + \\ \frac{1}{2}(\langle 0|X|0^{2R}\rangle + \langle 0^{2L}|X|0\rangle + 2\langle 0|X(^2\kappa)|0\rangle)^1S_j + \\ \frac{1}{2}\langle 0|X|0^{1R}\rangle^2S_j + \frac{1}{2}\sum_n {}^1S_n\,{}^2S_n^*\langle j|X|0\rangle \end{aligned} \tag{53}$$

$$\begin{aligned} X^{[3]}{}_{j,l_1l_2}[q_j]\alpha_{l_1}\alpha_{l_2} = \frac{1}{2}\langle 0|[q_j,X(^1\kappa,{}^2\kappa)]|0\rangle + \\ \langle 0|[q_j,X(^2\kappa)]|0^{1R}\rangle + \langle 0^{1L}|[q_j,X(^2\kappa)]|0\rangle + \frac{1}{2}(\langle 0^{2L}|[q_j,X]|0^{1R}\rangle + \\ \langle 0^{1L}|[q_j,X]|0^{2R}\rangle) + \frac{1}{2}\langle 0|[q_j,X]|0\rangle\sum_n(^2S_n^*\,{}^1S_n + {}^2S_n\,{}^1S_n^*) \end{aligned} \tag{54}$$

$$\begin{aligned} & X^{[4]}{}_{j,l_1l_2l_3}[q_j]\alpha_{l_1}\alpha_{l_2}\alpha_{l_3} = \\ & -\frac{1}{6}\langle 0|[q_j,X(^1\kappa,{}^2\kappa,{}^3\kappa)]|0\rangle - \frac{1}{2}(\langle 0|[q_j,X(^2\kappa,{}^3\kappa)]|0^{1R}\rangle + \\ & \qquad \langle 0^{1L}|[q_j,X(^2\kappa,{}^3\kappa)]|0\rangle) \\ & -\frac{1}{2}(\langle 0^{2L}|[q_j,X(^3\kappa)]|0^{1R}\rangle + \langle 0^{1L}|[q_j,X(^3\kappa)]|0^{2R}\rangle) \\ & -\frac{1}{2}\langle 0|[q_j,X(^3\kappa)]|0\rangle\sum_n(^2S_n^{*1}S_n + {}^2S_n\,{}^1S_n^*) \\ & -\frac{1}{6}\sum_n{}^3S_n(^2S_n^*\langle 0|[q_j,X]|0^{1R}\rangle + {}^1S_n^*\langle 0|[q_j,X]|0^{2R}\rangle) \\ & -\frac{1}{6}\sum_n{}^3S_n^*(^1S_n\langle 0^{2L}|[q_j,X]|0\rangle + {}^2S_n\langle 0^{1L}|[q_j,X]|0\rangle) \\ & -\frac{1}{6}(\langle 0|[q_j,X]|0^{3R}\rangle + \langle 0^{3L}|[q_j,X]|0\rangle)\sum_n(^2S_n^{*1}S_n + {}^2S_n\,{}^1S_n^*) \end{aligned} \tag{55}$$

$$\begin{aligned} & A_{j,l_1l_2l_3}^{[4]}[R_j^\dagger]\alpha_{l_1}\alpha_{l_2}\alpha_{l_3} = \\ & \frac{1}{6}\langle 0|A(^1\kappa,{}^2\kappa,{}^3\kappa)|j\rangle \\ & +\frac{1}{2}(\langle 0^{1L}|A(^2\kappa,{}^3\kappa)|j\rangle - {}^1S_j^*\langle 0|A(^2\kappa,{}^3\kappa)|0\rangle) \\ & -\frac{1}{2}(\langle 0|A(^3\kappa)|0^{2R}\rangle + \langle 0^{2L}|A(^3\kappa)|0\rangle)^1S_j^* \\ & -\frac{1}{2}\,{}^2S_j^*\langle 0^{1L}|A(^3\kappa)|0\rangle + \frac{1}{2}\sum_n{}^1S_n^*\,{}^2S_n\langle 0|A(^3\kappa)|j\rangle \\ & -\frac{1}{6}(\langle 0^{3L}|A|0^{2R}\rangle + \langle 0^{2L}|A|0^{3R}\rangle)^1S_j^* \\ & -\frac{1}{6}\sum_n(^3S_n^*\,{}^2S_n + {}^3S_n\,{}^2S_n^*)\langle 0|A|0\rangle^1S_j^* \\ & -\frac{1}{6}(\langle 0^{1L}|A|0^{3R}\rangle + \langle 0|A|0\rangle\sum_n{}^3S_n\,{}^1S_n^*)^2S_j^* \\ & +\frac{1}{6}\sum_n{}^1S_n^*\,{}^2S_n(\langle 0^{3L}|A|j\rangle - {}^3S_j^*\langle 0|A|0\rangle) \end{aligned} \tag{17}$$

$$\begin{aligned} & A_{j,l_1l_2l_3}^{[4]}[R_j]\alpha_{l_1}\alpha_{l_2}\alpha_{l_3} = \\ & -\frac{1}{6}\langle j|A(^1\kappa,{}^2\kappa,{}^3\kappa)|0\rangle \\ & -\frac{1}{2}(\langle j|A(^2\kappa,{}^3\kappa)|0^{1R}\rangle + {}^1S_j\langle 0|A(^2\kappa,{}^3\kappa)|0\rangle) \\ & -\frac{1}{2}(\langle 0|A(^3\kappa)|0^{2R}\rangle + \langle 0^{2L}|A(^3\kappa)|0\rangle)^1S_j \\ & -\frac{1}{2}\langle 0|A(^3\kappa)|0^{1R}\rangle\,{}^2S_j - \frac{1}{2}\sum_n{}^2S_n^*\,{}^1S_n\langle j|A(^3\kappa)0\rangle \\ & -\frac{1}{6}(\langle 0^{3L}|A|0^{2R}\rangle + \langle 0^{2L}|A|0^{3R}\rangle)^1S_j \\ & -\frac{1}{6}\sum_n(^3S_n^*\,{}^2S_n + {}^3S_n\,{}^2S_n^*)\langle 0|A|0\rangle^1S_j \\ & -\frac{1}{6}(\langle 0^{3L}|A|0^{1R}\rangle + \sum_n{}^3S_n^*\,{}^1S_n\langle 0|A|0\rangle)^2S_j \\ & -\frac{1}{6}(\langle j|A|0^{3R}\rangle + {}^3S_j\langle 0|A|0\rangle)\sum_n{}^2S_n^*\,{}^1S_n \end{aligned} \tag{18}$$

$$\begin{aligned} & A_{j,l_1l_2l_3}^{[4]}[q_j]\alpha_{l_1}\alpha_{l_2}\alpha_{l_3} = \\ & -\frac{1}{6}\langle 0|[q_j,A(^1\kappa,{}^2\kappa,{}^3\kappa)]|0\rangle \\ & -\frac{1}{2}(\langle 0|[q_j,A(^2\kappa,{}^3\kappa)]|0^{1R}\rangle + \langle 0^{1L}|[q_j,A(^2\kappa,{}^3\kappa)]|0\rangle) \\ & -\frac{1}{2}(\langle 0^{2L}|[q_j, A(^3\kappa)]|0^{1R}\rangle + \langle 0^{1L}|[q_j, A(^3\kappa)]|0^{2R}\rangle) \\ & -\frac{1}{2}\langle 0|[q_j, A(^3\kappa)]|0\rangle\sum_n(^2S_n^*\,{}^1S_n + {}^2S_n\,{}^1S_n^*) \\ & -\frac{1}{6}\sum_n{}^3S_n(^2S_n^*\langle 0|[q_j, A]|0^{1R}\rangle + {}^1S_n^*\langle 0|[q_j, A]|0^{2R}\rangle) \\ & -\frac{1}{6}\sum_n{}^3S_n^*(^1S_n\langle 0^{2L}|[q_j, A]|0\rangle + {}^2S_n\langle 0^{1L}|[q_j, A]|0\rangle) \\ & -\frac{1}{6}(\langle 0|[q_j, A]|0^{3R}\rangle + \\ & \qquad \langle 0^{3L}|[q_j, A]|0\rangle)\sum_n(^2S_n^*\,{}^1S_n + {}^2S_n\,{}^1S_n^*) \end{aligned} \tag{19}$$

Furthermore, the expansion of eq 29 gives to third order:

$$D^{[0]} = \langle 0|D|0\rangle \tag{56}$$

$$D^{[1]}_{l_i}\alpha_{l_1} = -\langle 0|D({}^1\kappa)|0\rangle - \langle 0|D|0^{1R}\rangle - \langle 0^{1L}|D|0\rangle \tag{57}$$

$$\begin{aligned} D^{[2]}{}_{l_1 l_2}\alpha_{l_1}\alpha_{l_2} = {} & \frac{1}{2}\langle 0|D({}^1\kappa,{}^2\kappa)|0\rangle + \langle 0|D({}^2\kappa)|0^{1R}\rangle + \\ & \langle 0^{1L}|D({}^2\kappa)|0\rangle + \frac{1}{2}(\langle 0^{2L}|D|0^{1R}\rangle + \langle 0^{1L}|D|0^{2R}\rangle + \\ & \langle 0|D|0\rangle \sum_n ({}^2S_n^{*1}S_n + {}^2S_n{}^1S_n^*)) \end{aligned} \tag{58}$$

$$\begin{aligned} D^{[3]}_{h_1h_2h_3}\alpha_{h_1}\alpha_{h_2}\alpha_{h_3} = {} & \\ & -\frac{1}{6}\langle 0|D({}^1\kappa,{}^2\kappa,{}^3\kappa)|0\rangle \\ & -\frac{1}{2}(\langle 0|D({}^2\kappa,{}^3\kappa)|0^{1R}\rangle + \langle 0^{1L}|D({}^2\kappa,{}^3\kappa)|0\rangle) \\ & -\frac{1}{2}(\langle 0^{2L}|D({}^3\kappa)|0^{1R}\rangle + \langle 0^{1L}|D({}^3\kappa)|0^{2R}\rangle) \\ & -\frac{1}{2}\langle 0|D({}^3\kappa)|0\rangle \sum_n ({}^2S_n^{*1}S_n + {}^2S_n{}^1S_n^*) \\ & -\frac{1}{6}\sum_n {}^3S_n(\langle 0|D|0^{1R}\rangle{}^2S_n^* + \langle 0|D|0^{2R}\rangle{}^1S_n^*) \\ & -\frac{1}{6}\sum_n {}^3S_n^*(\langle 0^{1L}|D|0\rangle{}^2S_n + \langle 0^{2L}|D|0\rangle{}^1S_n) \\ & -\frac{1}{6}\sum_n ({}^2S_n^{*1}S_n + {}^2S_n{}^1S_n^*)(\langle 0|D|0^{3R}\rangle + \langle 0^{3L}|D|0\rangle) \end{aligned} \tag{59}$$

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