Frequency Dependent Nonlinear Optical Properties of Molecules: Formulation and Implementation in the HONDO Program

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This article summarizes the detailed equations for the time-dependent Hartree–Fock treatment of nonlinear properties for perturbations made up of a static electric field and an oscillating field. Explicit expressions for all nonlinear processes up to third order are obtained in terms of the density matrices at the same order. For processes at second and third order in perturbation, expressions in terms of lower order quantities are also obtained by applying the $(2n + 1)$ theorem of perturbation theory. The corresponding computer implementation in the HONDO program is described.

INTRODUCTION

Nonlinear optical properties of certain class of molecules, for example conjugated organic compounds and conducting polymers, hold great promises for future technology.[1] Materials having fast nonlinear optical responses can be used for optical signal processing, optical computers, and other optical devices.[2,3] These applications of nonlinear optical materials have created an immense interest in the search for new materials with enhanced optical nonlinearity.[2] As a result, an increasingly large number of experimental observations of the nonlinear optical phenomena such as electrooptic Pockels effect (EOPE), second harmonic generation (SHG), optical rectification (OR), DC-electric field induced (EFI)SHG, third harmonic generation (THG), optical Kerr effect (OKE), DC-electric field induced (EFI)OR, etc. are being reported for new materials with varied structures and dimensions.[1–10] However, the experimental observations are still made on the basis of ad hoc screening of candidate molecular systems. A better understanding of the origins of the nonlinear optical phenomena in terms of the electronic structure and the relationship between the molecular structure and nonlinear optical properties of materials may offer a more desirable alternative to this ad hoc procedure. In this context, quantum mechanical studies of the nonlinear properties of materials may play an important role. Indeed such studies can give a priori information of the nonlinear properties of a large class of molecules. In particular extensive ab initio correlated results have been published for small molecules by Bartlett et al.[11–13] These studies deal with effects of electron correlation, molecular vibrations, and frequency dependence. For larger molecular systems, theoretical studies have been limited to approximate levels of theory.[14–18] Though these studies have provided some useful qualitative understanding of the structure-property relationship in systems such as conjugated polymers, the level of reliability of these techniques is still in doubt as they are parameterized for different electronic properties. With increasing computational capabilities, however, more accurate theoretical treatments of the nonlinear optical properties of rather large organic and polymeric materials[19–22] are becoming available. For example, Hurst et al.[21] have recently calculated the static polarizability and the first and the second hyperpolarizabilities of polyenes containing up to 22 carbon atoms. The goal of the present study is to extend these authors' work to the calculation of frequency dependent (hyper)-polarizabilities.

At the ab initio level, some theoretical treatments of the frequency-dependent nonlinear optical processes are already available in the literature.[11,23,34] However, these treatments which are designed to be used for specific atomic or diatomic problems, have little general applicability for larger molecules. The most general treatment using time-dependent coupled perturbed Hartree–Fock (CPHF) approach[35] (also called TDHF approach) has been given by Sekino and Bartlett.[19] In the work of these authors, the CPHF equations are solved iteratively at each order of perturbation.

In what follows, we give a complete derivation of the analytical expressions for the nonlinear processes up to third order in perturbation. The formulation is similar to the one of Sekino and Bartlett

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but we have removed some inconsistencies. Here the expressions are given in a form that is readily suitable for programming. Most significantly we also present alternative expressions based on the $(2n+1)$ theorem of perturbation theory. Sekino and Bartlett[19] already mentioned the possibility of taking advantage of this theorem which leads to computational savings albeit at the cost of more complicated equations, as developed fully below. Accordingly, knowledge of the wave function through order n allows one to calculate the energy through order $(2n + 1)$.[31,36–39] This theorem has been exploited by Lazzeretti and Zanasi[40] and by Hurst et al.[21,41] for calculating static hyperpolarizability and second hyperpolarizability of molecules by time-independent CPHF method. Klingbeil et al.[31] have used the $(2n + 1)$ rule to calculate dynamic third-order effects such as THG and IDRI in atomic systems but their formulation is not easily applicable for calculation on extended molecules. In the present work, in addition to the expressions for iterative calculations, we give all expressions which satisfy the $(2n + 1)$ rule for all second and third order effects. The approach adopted in this work is similar to that of Klingbeil et al.[31]

BASIC THEORY

We consider the interaction of an N-electron closed shell molecule with an external electric field comprised of a monochromatic oscillating optical field and a static electric field. The perturbation due to the external electric field can be represented as

$$\lambda = E(e^{+i\omega t} + e^{-i\omega t} + 1). \tag{1}$$

For the exponential part of the electric field we use the notation

$$e^{\pm i\omega t} = (e^{+i\omega t} + e^{-i\omega t}),$$

so that the dipolar interaction hamiltonian for perturbation in eq. (1) can be written as

$$\mathcal{H}'(r, t) = \mu \cdot E(e^{\pm i\omega t} + 1), \tag{2}$$

where μ is the dipole moment operator defined as

$$\mu = -\sum_{j}^{N} (e \cdot r_j). \tag{2a}$$

In eq. (2a) e is the electronic charge and r_j is the position vector of the jth electron. The electronic part of the time-dependent Schrödinger equation (in atomic units) for the molecule can be written as

$$\left[\mathcal{H}^0(r) + \mathcal{H}'(r, t) - i\frac{\partial}{\partial t}\right]\Psi(r, t) = 0, \tag{3}$$

where

$$\mathcal{H}^0(r) = \sum_j \left(-\frac{1}{2}\nabla_j^2 - \sum_A \frac{Z_A}{r_{jA}} + \sum_{j<k}\frac{1}{r_{jk}}\right) \tag{4}$$

and $\Psi(r, t)$ is the time-dependent wave function of the system. In eq. (4) the summation over j runs over all N electrons and summation over A runs over all nuclei in the molecule. To solve eq. (3) we restrict $\Psi(r, t)$ to be a single Slater determinant, an antisymmetrized product of N time-dependent spin orbitals. Using Frenkel's variational principle[42] the time dependent Hartree–Fock (HF) equation corresponding to eq. (3) is given in matrix form as

$$FC - i\frac{\partial}{\partial t}SC = SC\varepsilon. \tag{5}$$

with

$$\frac{\partial}{\partial t}C^{\dagger}SC = 0, \tag{6}$$

where C is the time-dependent coefficient matrix of N spatial orbitals ϕ, (the spin function is integrated out) which are constructed from the basis functions χ as

$$\phi = \chi C. \tag{7}$$

S is the overlap matrix given by

$$S_{st}(1) = (\chi_s(1)|\chi_t(1)). \tag{8}$$

F is the Fock matrix given by

$$F = H + D[2J - K], \tag{9}$$

and ε is the Lagrangian multiplier matrix. In eq. (9) H is the one-electron integral matrix, D is the density matrix and J and K are the two-electron Coulomb and exchange supermatrices. The density matrix D is defined in terms of the MO coefficient matrices as

$$D = CnC^{\dagger}. \tag{10}$$

where n is the diagonal matrix of occupation numbers (here $n = 2$ for all occupied orbitals and $n = 0$ for the virtual orbitals). The one electron-integral matrix H and the two-electron integral matrices J and K are defined over the basis function as

$$H_{st}(1) = \left(\chi_s(1)\left|-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}\right|\chi_t(1)\right), \tag{11}$$

$$J_{stuv}(1, 2) = \left(\chi_s(1)\chi_t(1)\left|\frac{1}{r_{12}}\right|\chi_u(2)\chi_v(2)\right), \tag{12}$$

$$K_{stuv}(1, 2) = \left(\chi_s(1)\chi_u(1)\left|\frac{1}{r_{12}}\right|\chi_t(2)\chi_v(2)\right). \tag{13}$$

For a basis set χ that is independent of the external electric field,

$$S \equiv S^0, \tag{14}$$

$$J \equiv J^0, \tag{15}$$

and

$$K \equiv K^0. \tag{16}$$

where the superscript 0 indicates the unperturbed matrices. Expanding F, C, ε, and D in terms of the external perturbations $\lambda^a, \lambda^b, \lambda^c, \ldots$ and using eq. (1) we get expansions as a function of the magnitude and direction of the electric field as:

$$F = F^0 + E^a F^a + (2!)^{-1} E^a E^b F^{ab} + (3!)^{-1} E^a E^b E^c F^{abc} + \cdots, \tag{17a}$$

$$C = C^0 + E^a C^a + (2!)^{-1} E^a E^b C^{ab} + (3!)^{-1} E^a E^b E^c C^{abc} + \cdots, \tag{17b}$$

$$\varepsilon = \varepsilon^0 + E^a \varepsilon^a + (2!)^{-1} E^a E^b \varepsilon^{ab} + (3!)^{-1} E^a E^b E^c \varepsilon^{abc} + \cdots, \tag{17c}$$

$$D = D^0 + E^a D^a + (2!)^{-1} E^a E^b D^{ab} + (3!)^{-1} E^a E^b E^c D^{abc} + \cdots, \tag{17d}$$

where summation over repeated indices is implied. In the above equations superscripts a, b, c, etc. represent the *direction* of the perturbation while their number indicates the *order* of the perturbation. Thus, for example,

$$F^a = F_a^{(1)}; \quad (a = x, y, z), \tag{18a}$$

$$F^{ab} = F_{ab}^{(2)}; \quad (a, b = x, y, z), \tag{18b}$$

$$F^{abc} = F_{abc}^{(3)}; \quad (a, b, c = x, y, z). \tag{18c}$$

The perturbed matrices in eqs. (17a)–(17d) are given by

$$F^a = e^{\pm i\omega t} F^a(\pm\omega) + F^a(0), \tag{19a}$$

$$F^{ab} = e^{\pm 2i\omega t} F^{ab}(\pm\omega, \pm\omega) + e^{\pm i\omega t}\{F^{ab}(0, \pm\omega) + F^{ab}(\pm\omega, 0)\} + F^{ab}(\pm\omega, \mp\omega) + F^{ab}(0, 0), \tag{19b}$$

$$\begin{aligned} F^{abc} = {} & e^{\pm 3i\omega t} F^{abc}(\pm\omega, \pm\omega, \pm\omega) \\ & + e^{\pm 2i\omega t}\{F^{abc}(0, \pm\omega, \pm\omega) \\ & + F^{abc}(\pm\omega, 0, \pm\omega) \\ & + F^{abc}(\pm\omega, \pm\omega, 0)\} \\ & + e^{\pm i\omega t}\{F^{abc}(\pm\omega, \pm\omega, \mp\omega) \\ & + F^{abc}(\pm\omega, \mp\omega, \pm\omega) \\ & + F^{abc}(\mp\omega, \pm\omega, \pm\omega)\} \\ & + e^{\pm i\omega t}\{F^{abc}(0, 0, \pm\omega) \\ & + F^{abc}(0, \pm\omega, 0) + F^{abc}(\pm\omega, 0, 0)\} \\ & + \{F^{abc}(0, \pm\omega, \mp\omega) + F^{abc}(\pm\omega, 0, \mp\omega) \\ & + F^{abc}(\pm\omega, \mp\omega, 0)\} \\ & + F^{abc}(0, 0, 0), \end{aligned} \tag{19c}$$

with similar expressions for C, D, and ε. The notation in eqs. (19a) to (19c) implies that one uses all phase signs uniformly; for example the first term in the right hand side of eq. (19b) is a short handed notation for $e^{+2i\omega t} F^{ab}(+\omega, +\omega) + e^{-2i\omega t} F^{ab}(-\omega, -\omega)$. No other phase combination exists. This convention is used throughout.

The CPHF Equations

Substituting eqs. (17a) to (17c) in eq. (5) and equating coefficients of same exponential terms on both sides leads to various CPHF equations in different orders as given in Table I. It can be noted that unlike the expressions given by Sekino and Bartlett,[19] all expressions for dynamic interactions (for nonzero ω) as given above, collapse to their static counterparts as $\omega \to 0$. In this notation, the CPHF equations for the static case ($\omega = 0$) up to the second order in perturbation are similar to those given by Hurst and Dupuis.[41] In the work of these authors the third order CPHF equations are not solved explicitly, rather the lower order solutions of the CPHF equation are used to get the third order property. We apply later the same strategy to the dynamic cases.

The Normalization Equations

Since the approach for solving the CPHF equations involves an interative technique which requires various intermediate quantities obtained from the orthonormalization condition (eq. (6)), it is useful to write the orthonormalization equations for each order of expansion. To this end we substitute eq. (17b) in eq. (6) and separate the factors of the different exponential terms, keeping in mind that the complex conjugate of $e^{\pm i\omega t}$ is $e^{\mp i\omega t}$. This gives the equations in different order of perturbation listed in Table II.

The Density Matrix

The density matrix corresponding to the perturbed coefficient matrix **C** is obtained by substituting eq. (17b) into eq. (10) and collecting the terms order by order. This results in the expressions given in Table III for density matrices in different order of perturbation. Once the density matrices have been obtained, the polarizabilities and hyperpolarizabilities corresponding to different interaction can be obtained in the dipole approximation from the dipole moment matrices H^a ($a = x, y, z$) defined as

$$H_{st}^a(1) = -(\chi_s(1)|e \cdot a_1|\chi_t(1)), \tag{20}$$

and from the density matrices, using the expressions of Table IV (a detailed derivation is given in Appendix A): In Table IV *Tr* stands for trace as defined in Appendix A.

ITERATIVE SOLUTION OF THE CPHF EQUATIONS

The zeroth order HF equation is solved in the standard manner through the self-consistent-field (SCF) method. For the first order the Fock matrix has the following form

$$F^a(\pm\omega) = H^a + D^a(\pm\omega)[2J^0 - K^0] \tag{21a}$$

$$F^a(0) = H^a + D^a(0)[2J^0 - K^0] \tag{21b}$$

Table I. The CPHF equations

The zeroth order

$$F^0C^0 = S^0C^0\varepsilon^0 \tag{I}$$

The first order

$$F^a(\pm\omega)C^0 + F^0C^a(\pm\omega) \pm \omega S^0C^a(\pm\omega) = S^0C^a(\pm\omega)\varepsilon^0 + S^0C^0\varepsilon^a(\pm\omega) \tag{I-1a}$$

$$F^a(0)C^0 + F^0C^a(0) = S^0C^a(0)\varepsilon^0 + S^0C^0\varepsilon^a(0) \tag{I-1b}$$

The second order

$$\begin{aligned} &F^{ab}(\pm\omega, \pm\omega)C^0 + F^a(\pm\omega)C^b(\pm\omega) + F^b(\pm\omega)C^a(\pm\omega) + F^0C^{ab}(\pm\omega, \pm\omega) \pm 2\omega S^0C^{ab}(\pm\omega, \pm\omega) \\ &\quad = S^0C^{ab}(\pm\omega, \pm\omega)\varepsilon^0 + S^0C^a(\pm\omega)\varepsilon^b(\pm\omega) + S^0C^b(\pm\omega)\varepsilon^a(\pm\omega) + S^0C^0\varepsilon^{ab}(\pm\omega, \pm\omega) \end{aligned} \tag{I-2a}$$

$$\begin{aligned} &F^{ab}(0, \pm\omega)C^0 + F^a(0)C^b(\pm\omega) + F^b(\pm\omega)C^a(0) + F^0C^{ab}(0, \pm\omega) \pm \omega S^0C^{ab}(0, \pm\omega) \\ &\quad = S^0C^{ab}(0, \pm\omega)\varepsilon^0 + S^0C^a(0)\varepsilon^b(\pm\omega) + S^0C^b(\pm\omega)\varepsilon^a(0) + S^0C^0\varepsilon^{ab}(0, \pm\omega) \end{aligned} \tag{I-2b}$$

$$\begin{aligned} &F^{ab}(\pm\omega, \mp\omega)C^0 + F^a(\pm\omega)C^b(\mp\omega) + F^b(\mp\omega)C^a(\pm\omega) + F^0C^{ab}(\pm\omega, \mp\omega) \\ &\quad = S^0C^{ab}(\pm\omega, \mp\omega)\varepsilon^0 + S^0C^a(\pm\omega)\varepsilon^b(\mp\omega) + S^0C^b(\mp\omega)\varepsilon^a(\pm\omega) + S^0C^0\varepsilon^{ab}(\pm\omega, \mp\omega) \end{aligned} \tag{I-2c}$$

$$\begin{aligned} &F^{ab}(0, 0)C^0 + F^a(0)C^b(0) + F^b(0)C^a(0) + F^0C^{ab}(0, 0) \\ &\quad = S^0C^{ab}(0, 0)\varepsilon^0 + S^0C^a(0)\varepsilon^b(0) + S^0C^b(0)\varepsilon^a(0) + S^0C^0\varepsilon^{ab}(0, 0) \end{aligned} \tag{I-2d}$$

The third order

$$\begin{aligned} &F^{abc}(\pm\omega, \pm\omega, \pm\omega)C^0 + F^a(\pm\omega)C^{bc}(\pm\omega, \pm\omega) + F^{bc}(\pm\omega, \pm\omega)C^a(\pm\omega) \\ &\quad + F^b(\pm\omega)C^{ac}(\pm\omega, \pm\omega) + F^{ac}(\pm\omega, \pm\omega)C^b(\pm\omega) + F^c(\pm\omega)C^{ab}(\pm\omega, \pm\omega) + F^{ab}(\pm\omega, \pm\omega)C^c(\pm\omega) \\ &\quad + F^0C^{abc}(\pm\omega, \pm\omega, \pm\omega) \pm 3\omega S^0C^{abc}(\pm\omega, \pm\omega, \pm\omega) \\ &= S^0C^{abc}(\pm\omega, \pm\omega, \pm\omega)\varepsilon^0 + S^0C^a(\pm\omega)\varepsilon^{bc}(\pm\omega, \pm\omega) + S^0C^{bc}(\pm\omega, \pm\omega)\varepsilon^a(\pm\omega) \\ &\quad + S^0C^b(\pm\omega)\varepsilon^{ac}(\pm\omega, \pm\omega) + S^0C^{ac}(\pm\omega, \pm\omega)\varepsilon^b(\pm\omega) + S^0C^c(\pm\omega)\varepsilon^{ab}(\pm\omega, \pm\omega) \\ &\quad + S^0C^{ab}(\pm\omega, \pm\omega)\varepsilon^c(\pm\omega) + S^0C^0\varepsilon^{abc}(\pm\omega, \pm\omega, \pm\omega) \end{aligned} \tag{I-3a}$$

$$\begin{aligned} &F^{abc}(0, \pm\omega, \pm\omega)C^0 + F^a(0)C^{bc}(\pm\omega, \pm\omega) + F^{bc}(\pm\omega, \pm\omega)C^a(0) \\ &\quad + F^b(\pm\omega)C^{ac}(0, \pm\omega) + F^{ac}(0, \pm\omega)C^b(\pm\omega) + F^c(\pm\omega)C^{ab}(0, \pm\omega) \\ &\quad + F^{ab}(0, \pm\omega)C^c(\pm\omega) + F^0C^{abc}(0, \pm\omega, \pm\omega) \pm 2\omega S^0C^{abc}(0, \pm\omega, \pm\omega) \\ &= S^0C^{abc}(0, \pm\omega, \pm\omega)\varepsilon^0 + S^0C^a(0)\varepsilon^{bc}(\pm\omega, \pm\omega) + S^0C^{bc}(\pm\omega, \pm\omega)\varepsilon^a(0) \\ &\quad + S^0C^b(\pm\omega)\varepsilon^{ac}(0, \pm\omega) + S^0C^{ac}(0, \pm\omega)\varepsilon^b(\pm\omega) + S^0C^c(\pm\omega)\varepsilon^{ab}(0, \pm\omega) \\ &\quad + S^0C^{ab}(0, \pm\omega)\varepsilon^c(\pm\omega) + S^0C^0\varepsilon^{abc}(0, \pm\omega, \pm\omega) \end{aligned} \tag{I-3b}$$

$$\begin{aligned} &F^{abc}(\pm\omega, \pm\omega, \mp\omega)C^0 + F^a(\pm\omega)C^{bc}(\pm\omega, \mp\omega) + F^{bc}(\pm\omega, \mp\omega)C^a(\pm\omega) \\ &\quad + F^b(\pm\omega)C^{ac}(\pm\omega, \mp\omega) + F^{ac}(\pm\omega, \mp\omega)C^b(\pm\omega) + F^c(\mp\omega)C^{ab}(\pm\omega, \pm\omega) \\ &\quad + F^{ab}(\pm\omega, \pm\omega)C^c(\mp\omega) + F^0C^{abc}(\pm\omega, \pm\omega, \mp\omega) \pm \omega S^0C^{abc}(\pm\omega, \pm\omega, \mp\omega) \\ &= S^0C^{abc}(\pm\omega, \pm\omega, \mp\omega)\varepsilon^0 + S^0C^a(\pm\omega)\varepsilon^{bc}(\pm\omega, \mp\omega) + S^0C^{bc}(\pm\omega, \mp\omega)\varepsilon^a(\pm\omega) \\ &\quad + S^0C^b(\pm\omega)\varepsilon^{ac}(\pm\omega, \mp\omega) + S^0C^{ac}(\pm\omega, \mp\omega)\varepsilon^b(\pm\omega) + S^0C^c(\mp\omega)\varepsilon^{ab}(\pm\omega, \pm\omega) \\ &\quad + S^0C^{ab}(\pm\omega, \pm\omega)\varepsilon^c(\mp\omega) + S^0C^0\varepsilon^{abc}(\pm\omega, \pm\omega, \mp\omega) \end{aligned} \tag{I-3c}$$

$$\begin{aligned} &F^{abc}(0, 0, \pm\omega)C^0 + F^a(0)C^{bc}(0, \pm\omega) + F^{bc}(0, \pm\omega)C^a(0) + F^b(0)C^{ac}(0, \pm\omega) + F^{ac}(0, \pm\omega)C^b(0) \\ &\quad + F^c(\pm\omega)C^{ab}(0, 0) + F^{ab}(0, 0)C^c(\pm\omega) + F^0C^{abc}(0, 0, \pm\omega) \pm \omega S^0C^{abc}(0, 0, \pm\omega) \\ &= S^0C^{abc}(0, 0, \pm\omega)\varepsilon^0 + S^0C^a(0)\varepsilon^{bc}(0, \pm\omega) + S^0C^{bc}(0, \pm\omega)\varepsilon^a(0) + S^0C^b(0)\varepsilon^{ac}(0, \pm\omega) + S^0C^{ac}(0, \pm\omega)\varepsilon^b(0) \\ &\quad + S^0C^c(\pm\omega)\varepsilon^{ab}(0, 0) + S^0C^{ab}(0, 0)\varepsilon^c(\pm\omega) + S^0C^0\varepsilon^{abc}(0, 0, \pm\omega) \end{aligned} \tag{I-3d}$$

$$\begin{aligned} &F^{abc}(0, \pm\omega, \mp\omega)C^0 + F^a(0)C^{bc}(\pm\omega, \mp\omega) + F^{bc}(\pm\omega, \mp\omega)C^a(0) + F^b(\pm\omega)C^{ac}(0, \mp\omega) + F^{ac}(0, \mp\omega)C^b(\pm\omega) \\ &\quad + F^c(\mp\omega)C^{ab}(0, \pm\omega) + F^{ab}(0, \pm\omega)C^c(\mp\omega) + F^0C^{abc}(0, \pm\omega, \mp\omega) \\ &= S^0C^{abc}(0, \pm\omega, \mp\omega)\varepsilon^0 + S^0C^a(0)\varepsilon^{bc}(\pm\omega, \mp\omega) + S^0C^{bc}(\pm\omega, \mp\omega)\varepsilon^a(0) \\ &\quad + S^0C^b(\pm\omega)\varepsilon^{ac}(0, \mp\omega) + S^0C^{ac}(0, \mp\omega)\varepsilon^b(\pm\omega) + S^0C^c(\mp\omega)\varepsilon^{ab}(0, \pm\omega) \\ &\quad + S^0C^{ab}(0, \pm\omega)\varepsilon^c(\mp\omega) + S^0C^0\varepsilon^{abc}(0, \pm\omega, \mp\omega) \end{aligned} \tag{I-3e}$$

$$\begin{aligned} &F^{abc}(0, 0, 0)C^0 + F^a(0)C^{bc}(0, 0) + F^{bc}(0, 0)C^a(0) + F^b(0)C^{ac}(0, 0) + F^{ac}(0, 0)C^b(0) \\ &\quad + F^c(0)C^{ab}(0, 0) + F^{ab}(0, 0)C^c(0) + F^0C^{abc}(0, 0, 0) \\ &= S^0C^{abc}(0, 0, 0)\varepsilon^0 + S^0C^a(0)\varepsilon^{bc}(0, 0) + S^0C^{bc}(0, 0)\varepsilon^a(0) + S^0C^b(0)\varepsilon^{ac}(0, 0) + S^0C^{ac}(0, 0)\varepsilon^b(0) \\ &\quad + S^0C^c(0)\varepsilon^{ab}(0, 0) + S^0C^{ab}(0, 0)\varepsilon^c(0) + S^0C^0\varepsilon^{abc}(0, 0, 0) \end{aligned} \tag{I-3f}$$

Since the dipole moment matrix H^a has no terms higher than the first order, the second-and higher-order Fock matrices are of the form

$$F^{ab}(\pm\omega, \pm\omega) = D^{ab}(\pm\omega, \pm\omega)[2J^0 - K^0] \tag{22a}$$

$$F^{ab}(0, \pm\omega) = D^{ab}(0, \pm\omega)[2J^0 - K^0] \tag{22b}$$

$$F^{ab}(\pm\omega, \mp\omega) = D^{ab}(\pm\omega, \mp\omega)[2J^0 - K^0] \tag{22c}$$

$$F^{ab}(0, 0) = D^{ab}(0, 0)[2J^0 - K^0] \tag{22d}$$

$$F^{abc}(\pm\omega, \pm\omega, \pm\omega) = D^{abc}(\pm\omega, \pm\omega, \pm\omega)[2J^0 - K^0] \tag{23a}$$

Table II. Normalization equations.

The zeroth order

$$C^{0\dagger}S^0C^0 = 1 \quad \text{(II)}$$

The first order

$$C^{0\dagger}S^0C^a(\pm\omega) + C^{a\dagger}(\mp\omega)S^0C^0 = 0 \quad \text{(II-1a)}$$

$$C^{0\dagger}S^0C^a(0) + C^{a\dagger}(0)S^0C^0 = 0 \quad \text{(II-1b)}$$

The second order

$$C^{0\dagger}S^0C^{ab}(\pm\omega, \pm\omega) + C^{a\dagger}(\mp\omega)S^0C^b(\pm\omega) + C^{b\dagger}(\mp\omega)S^0C^a(\pm\omega) + C^{ab\dagger}(\mp\omega, \mp\omega)S^0C^0 = 0 \quad \text{(II-2a)}$$

$$C^{0\dagger}S^0C^{ab}(0, \pm\omega) + C^{a\dagger}(0)S^0C^b(\pm\omega) + C^{b\dagger}(\mp\omega)S^0C^a(0) + C^{ab\dagger}(0, \mp\omega)S^0C^0 = 0 \quad \text{(II-2b)}$$

$$C^{0\dagger}S^0C^{ab}(\pm\omega, \mp\omega) + C^{a\dagger}(\mp\omega)S^0C^b(\mp\omega) + C^{b\dagger}(\pm\omega)S^0C^a(\pm\omega) + C^{ab\dagger}(\mp\omega, \pm\omega)S^0C^0 = 0 \quad \text{(II-2c)}$$

$$C^{0\dagger}S^0C^{ab}(0, 0) + C^{a\dagger}(0)S^0C^b(0) + C^{b\dagger}(0)S^0C^a(0) + C^{ab\dagger}(0, 0)S^0C^0 = 0 \quad \text{(II-2d)}$$

The third order

$$C^{0\dagger}S^0C^{abc}(\pm\omega, \pm\omega, \pm\omega) + C^{a\dagger}(\mp\omega)S^0C^{bc}(\pm\omega, \pm\omega) + C^{bc\dagger}(\mp\omega, \mp\omega)S^0C^a(\pm\omega) + C^{b\dagger}(\mp\omega)S^0C^{ac}(\pm\omega, \pm\omega) \\ + C^{ac\dagger}(\mp\omega, \mp\omega)S^0C^b(\pm\omega) + C^{c\dagger}(\mp\omega)S^0C^{ab}(\pm\omega, \pm\omega) + C^{ab\dagger}(\mp\omega, \mp\omega)S^0C^c(\pm\omega) + C^{abc\dagger}(\mp\omega, \mp\omega, \mp\omega)S^0C^0 = 0 \quad \text{(II-3a)}$$

$$C^{0\dagger}S^0C^{abc}(0, \pm\omega, \pm\omega) + C^{a\dagger}(0)S^0C^{bc}(\pm\omega, \pm\omega) + C^{bc\dagger}(\mp\omega, \mp\omega)S^0C^a(0) + C^{b\dagger}(\mp\omega)S^0C^{ac}(0, \pm\omega) \\ + C^{ac\dagger}(0, \mp\omega)S^0C^b(\pm\omega) + C^{c\dagger}(\mp\omega)S^0C^{ab}(0, \pm\omega) + C^{ab\dagger}(0, \mp\omega)S^0C^c(\pm\omega) + C^{abc\dagger}(0, \mp\omega, \mp\omega)S^0C^0 = 0 \quad \text{(II-3b)}$$

$$C^{0\dagger}S^0C^{abc}(\pm\omega, \pm\omega, \mp\omega) + C^{a\dagger}(\mp\omega)S^0C^{bc}(\pm\omega, \mp\omega) + C^{bc\dagger}(\mp\omega, \pm\omega)S^0C^a(\pm\omega) + C^{b\dagger}(\mp\omega)S^0C^{ac}(\pm\omega, \mp\omega) \\ + C^{ac\dagger}(\mp\omega, \pm\omega)S^0C^b(\pm\omega) + C^{c\dagger}(\pm\omega)S^0C^{ab}(\pm\omega, \pm\omega) + C^{ab\dagger}(\mp\omega, \mp\omega)S^0C^c(\mp\omega) + C^{abc\dagger}(\mp\omega, \mp\omega, \pm\omega)S^0C^0 = 0 \quad \text{(II-3c)}$$

$$C^{0\dagger}S^0C^{abc}(0, 0, \pm\omega) + C^{a\dagger}(0)S^0C^{bc}(0, \pm\omega) + C^{bc\dagger}(0, \mp\omega)S^0C^a(0) + C^{b\dagger}(0)S^0C^{ac}(0, \pm\omega) \\ + C^{ac\dagger}(0, \mp\omega)S^0C^b(0) + C^{c\dagger}(\mp\omega)S^0C^{ab}(0, 0) + C^{ab\dagger}(0, 0)S^0C^c(\pm\omega) + C^{abc\dagger}(0, 0, \mp\omega)S^0C^0 = 0 \quad \text{(II-3d)}$$

$$C^{0\dagger}S^0C^{abc}(0, \pm\omega, \mp\omega) + C^{a\dagger}(0)S^0C^{bc}(\pm\omega, \mp\omega) + C^{bc\dagger}(\mp\omega, \pm\omega)S^0C^a(0) + C^{b\dagger}(\mp\omega)S^0C^{ac}(0, \mp\omega) \\ + C^{ac\dagger}(0, \pm\omega)S^0C^b(\pm\omega) + C^{c\dagger}(\pm\omega)S^0C^{ab}(0, \pm\omega) + C^{ab\dagger}(0, \mp\omega)S^0C^c(\mp\omega) + C^{abc\dagger}(0, \mp\omega, \pm\omega)S^0C^0 = 0 \quad \text{(II-3e)}$$

$$C^{0\dagger}S^0C^{abc}(0, 0, 0) + C^{a\dagger}(0)S^0C^{bc}(0, 0) + C^{bc\dagger}(0, 0)S^0C^a(0) + C^{b\dagger}(0)S^0C^{ac}(0, 0) \\ + C^{ac\dagger}(0, 0)S^0C^b(0) + C^{c\dagger}(0)S^0C^{ab}(0, 0) + C^{ab\dagger}(0, 0)S^0C^c(0) + C^{abc\dagger}(0, 0, 0)S^0C^0 = 0 \quad \text{(II-3f)}$$

$$F^{abc}(0, \pm\omega, \pm\omega) = D^{abc}(0, \pm\omega, \pm\omega)[2J^0 - K^0] \quad (23b)$$

$$F^{abc}(\pm\omega, \pm\omega, \mp\omega) = D^{abc}(\pm\omega, \pm\omega, \mp\omega)[2J^0 - K^0] \quad (23c)$$

$$F^{abc}(0, 0, \pm\omega) = D^{abc}(0, 0, \pm\omega)[2J^0 - K^0] \quad (23d)$$

$$F^{abc}(0, \pm\omega, \mp\omega) = D^{abc}(0, \pm\omega, \mp\omega)[2J^0 - K^0] \quad (23e)$$

$$F^{abc}(0, 0, 0) = D^{abc}(0, 0, 0)[2J^0 - K^0] \quad (23f)$$

Thus the construction of the Fock matrices proceeds from the perturbed density matrices which require the zeroth order and perturbed MO coefficient matrices (eqs. (III-1a)–(III-3f)) which in turn are the solutions of the corresponding order and of the lower order CPHF equations (Table I). Therefore, an iterative procedure similar to the one used to solve the zeroth order equation can be used to solve the higher order equations with the help of some additional parameters as defined below. We define the transformation matrices U as

$$C^a(\pm\omega) = C^0U^a(\pm\omega) \quad (24a)$$

$$C^a(0) = C^0U^a(0) \quad (24b)$$

$$C^{ab}(\pm\omega, \pm\omega) = C^0U^{ab}(\pm\omega, \pm\omega) \quad (25a)$$

$$C^{ab}(0, \pm\omega) = C^0U^{ab}(0, \pm\omega) \quad (25b)$$

$$C^{ab}(\pm\omega, \mp\omega) = C^0U^{ab}(\pm\omega, \mp\omega) \quad (25c)$$

$$C^{ab}(0, 0) = C^0U^{ab}(0, 0) \quad (25d)$$

$$C^{abc}(\pm\omega, \pm\omega, \pm\omega) = C^0U^{abc}(\pm\omega, \pm\omega, \pm\omega) \quad (26a)$$

$$C^{abc}(0, \pm\omega, \pm\omega) = C^0U^{abc}(0, \pm\omega, \pm\omega) \quad (26b)$$

$$C^{abc}(\pm\omega, \pm\omega, \mp\omega) = C^0U^{abc}(\pm\omega, \pm\omega, \mp\omega) \quad (26c)$$

$$C^{abc}(0, 0, \pm\omega) = C^0U^{abc}(0, 0, \pm\omega) \quad (26d)$$

$$C^{abc}(0, \pm\omega, \mp\omega) = C^0U^{abc}(0, \pm\omega, \mp\omega) \quad (26e)$$

$$C^{abc}(0, 0, 0) = C^0U^{abc}(0, 0, 0) \quad (26f)$$

and the G matrices expressed in the MO basis

$$G^a(\pm\omega) = C^{0\dagger}F^a(\pm\omega)C^0 \quad (27a)$$

$$G^a(0) = C^{0\dagger}F^a(0)C^0 \quad (27b)$$

$$G^{ab}(\pm\omega, \pm\omega) = C^{0\dagger}F^{ab}(\pm\omega, \pm\omega)C^0 \quad (28a)$$

$$G^{ab}(0, \pm\omega) = C^{0\dagger}F^{ab}(0, \pm\omega)C^0 \quad (28b)$$

$$G^{ab}(\pm\omega, \mp\omega) = C^{0\dagger}F^{ab}(\pm\omega, \mp\omega)C^0 \quad (28c)$$

$$G^{ab}(0, 0) = C^{0\dagger}F^{ab}(0, 0)C^0 \quad (28d)$$

Table III. Density matrix equations.

The zeroth order

$$D^0 = C^0 n C^{0\dagger} \tag{III}$$

The first order

$$D^a(\pm\omega) = C^a(\pm\omega) n C^{0\dagger} + C^0 n C^{a\dagger}(\mp\omega) \tag{III-1a}$$

$$D^a(0) = C^a(0) n C^{0\dagger} + C^0 n C^{a\dagger}(0) \tag{III-1b}$$

The second order

$$D^{ab}(\pm\omega, \pm\omega) = C^{ab}(\pm\omega, \pm\omega) n C^{0\dagger} + C^a(\pm\omega) n C^{b\dagger}(\mp\omega) + C^b(\pm\omega) n C^{a\dagger}(\mp\omega) + C^0 n C^{ab\dagger}(\mp\omega, \mp\omega) \tag{III-2a}$$

$$D^{ab}(0, \pm\omega) = C^{ab}(0, \pm\omega) n C^{0\dagger} + C^a(0) n C^{b\dagger}(\mp\omega) + C^b(\pm\omega) n C^{a\dagger}(0) + C^0 n C^{ab\dagger}(0, \mp\omega) \tag{III-2b}$$

$$D^{ab}(\pm\omega, \mp\omega) = C^{ab}(\pm\omega, \mp\omega) n C^{0\dagger} + C^a(\pm\omega) n C^{b\dagger}(\pm\omega) + C^b(\mp\omega) n C^{a\dagger}(\mp\omega) + C^0 n C^{ab\dagger}(\mp\omega, \pm\omega) \tag{III-2c}$$

$$D^{ab}(0, 0) = C^{ab}(0, 0) n C^{0\dagger} + C^a(0) n C^{b\dagger}(0) + C^b(0) n C^{a\dagger}(0) + C^0 n C^{ab\dagger}(0, 0) \tag{III-2d}$$

The third order

$$\begin{aligned} D^{abc}(\pm\omega, \pm\omega, \pm\omega) = {} & C^{abc}(\pm\omega, \pm\omega, \pm\omega) n C^{0\dagger} + C^a(\pm\omega) n C^{bc\dagger}(\mp\omega, \mp\omega) \\ & + C^{bc}(\pm\omega, \pm\omega) n C^{a\dagger}(\mp\omega) + C^b(\pm\omega) n C^{ac\dagger}(\mp\omega, \mp\omega) + C^{ac}(\pm\omega, \pm\omega) n C^{b\dagger}(\mp\omega) \\ & + C^c(\pm\omega) n C^{ab\dagger}(\mp\omega, \mp\omega) + C^{ab}(\pm\omega, \pm\omega) n C^{c\dagger}(\mp\omega) + C^0 n C^{abc\dagger}(\mp\omega, \mp\omega, \mp\omega) \end{aligned} \tag{III-3a}$$

$$\begin{aligned} D^{abc}(0, \pm\omega, \pm\omega) = {} & C^{abc}(0, \pm\omega, \pm\omega) n C^{0\dagger} + C^a(0) n C^{bc\dagger}(\mp\omega, \mp\omega) \\ & + C^{bc}(\pm\omega, \pm\omega) n C^{a\dagger}(0) + C^b(\pm\omega) n C^{ac\dagger}(0, \mp\omega) + C^{ac}(0, \pm\omega) n C^{b\dagger}(\mp\omega) \\ & + C^c(\pm\omega) n C^{ab\dagger}(0, \mp\omega) + C^{ab}(0, \pm\omega) n C^{c\dagger}(\mp\omega) + C^0 n C^{abc\dagger}(0, \mp\omega, \mp\omega) \end{aligned} \tag{III-3b}$$

$$\begin{aligned} D^{abc}(\pm\omega, \pm\omega, \mp\omega) = {} & C^{abc}(\pm\omega, \pm\omega, \mp\omega) n C^{0\dagger} + C^a(\pm\omega) n C^{bc\dagger}(\mp\omega, \pm\omega) \\ & + C^{bc}(\pm\omega, \mp\omega) n C^{a\dagger}(\mp\omega) + C^b(\pm\omega) n C^{ac\dagger}(\mp\omega, \pm\omega) + C^{ac}(\pm\omega, \mp\omega) n C^{b\dagger}(\mp\omega) \\ & + C^c(\mp\omega) n C^{ab\dagger}(\mp\omega, \mp\omega) + C^{ab}(\pm\omega, \pm\omega) n C^{c\dagger}(\pm\omega) + C^0 n C^{abc\dagger}(\mp\omega, \mp\omega, \pm\omega) \end{aligned} \tag{III-3c}$$

$$\begin{aligned} D^{abc}(0, 0, \pm\omega) = {} & C^{abc}(0, 0, \pm\omega) n C^{0\dagger} + C^a(0) n C^{bc\dagger}(0, \mp\omega) \\ & + C^{bc}(0, \pm\omega) n C^{a\dagger}(0) + C^b(0) n C^{ac\dagger}(0, \mp\omega) + C^{ac}(0, \pm\omega) n C^{b\dagger}(0) \\ & + C^c(\pm\omega) n C^{ab\dagger}(0, 0) + C^{ab}(0, 0) n C^{c\dagger}(\mp\omega) + C^0 n C^{abc\dagger}(0, 0, \mp\omega) \end{aligned} \tag{III-3d}$$

$$\begin{aligned} D^{abc}(0, \pm\omega, \mp\omega) = {} & C^{abc}(0, \pm\omega, \mp\omega) n C^{0\dagger} + C^a(0) n C^{bc\dagger}(\mp\omega, \pm\omega) \\ & + C^{bc}(\pm\omega, \mp\omega) n C^{a\dagger}(0) + C^b(\pm\omega) n C^{ac\dagger}(0, \pm\omega) + C^{ac}(0, \mp\omega) n C^{b\dagger}(\mp\omega) \\ & + C^c(\mp\omega) n C^{ab\dagger}(0, \mp\omega) + C^{ab}(0, \pm\omega) n C^{c\dagger}(\pm\omega) + C^0 n C^{abc\dagger}(0, \mp\omega, \pm\omega) \end{aligned} \tag{III-3e}$$

$$\begin{aligned} D^{abc}(0, 0, 0) = {} & C^{abc}(0, 0, 0) n C^{0\dagger} + C^a(0) n C^{bc\dagger}(0, 0) \\ & + C^{bc}(0, 0) n C^{a\dagger}(0) + C^b(0) n C^{ac\dagger}(0, 0) + C^{ac}(0, 0) n C^{b\dagger}(0) \\ & + C^c(0) n C^{ab\dagger}(0, 0) + C^{ab}(0, 0) n C^{c\dagger}(0) + C^0 n C^{abc\dagger}(0, 0, 0) \end{aligned} \tag{III-3f}$$

$$G^{abc}(\pm\omega, \pm\omega, \pm\omega) = C^{0\dagger} F^{abc}(\pm\omega, \pm\omega, +\omega) C^0 \tag{29a}$$

$$G^{abc}(0, \pm\omega, \pm\omega) = C^{0\dagger} F^{abc}(0, \pm\omega, \pm\omega) C^0 \tag{29b}$$

$$G^{abc}(\pm\omega, \pm\omega, \mp\omega) = C^{0\dagger} F^{abc}(\pm\omega, \pm\omega, \mp\omega) C^0 \tag{29c}$$

$$G^{abc}(0, 0, \pm\omega) = C^{0\dagger} F^{abc}(0, 0, \pm\omega) C^0 \tag{29d}$$

$$G^{abc}(0, \pm\omega, \mp\omega) = C^{0\dagger} F^{abc}(0, \pm\omega, \mp\omega) C^0 \tag{29e}$$

$$G^{abc}(0, 0, 0) = C^{0\dagger} F^{abc}(0, 0, 0) C^0 \tag{29f}$$

It should be noted that unlike for the static case the frequency-dependent F, D, ε, and U matrices are not symmetric and one has to construct the full matrices. However, the following relations hold

$$D^a(+\omega) = D^a(-\omega)^\dagger \tag{30}$$

$$D^{ab}(+\omega, +\omega) = D^{ab}(-\omega, -\omega)^\dagger \tag{31a}$$

$$D^{ab}(0, +\omega) = D^{ab}(0, -\omega)^\dagger \tag{31b}$$

$$D^{ab}(+\omega, -\omega) = D^{ab}(-\omega, +\omega)^\dagger \tag{31c}$$

$$D^{abc}(+\omega, +\omega, +\omega) = D^{abc}(-\omega, -\omega, -\omega)^\dagger \tag{32a}$$

$$D^{abc}(0, +\omega, +\omega) = D^{abc}(0, -\omega, -\omega)^\dagger \tag{32b}$$

$$D^{abc}(+\omega, +\omega, -\omega) = D^{abc}(-\omega, -\omega, +\omega)^\dagger \tag{32c}$$

$$D^{abc}(0, 0, +\omega) = D^{abc}(0, 0, -\omega)^\dagger \tag{32d}$$

$$D^{abc}(0, +\omega, -\omega) = D^{abc}(0, -\omega, +\omega)^\dagger \tag{32e}$$

with similar relationships for F, ε, and G matrices. Thus for a given pair of arguments, for example $(\pm\omega)$ one only needs to compute the F, D, ε, and G matrices for either $(+\omega)$ or $(-\omega)$.

The zeroth order coefficient matrix, C^0 is available from the SCF calculation, so that the problem of obtaining the perturbed coefficient matrices reduces to forming the transformation matrices, U. In what follows the U matrices are obtained iteratively from the CPHF equations and the orthonormalization equations.

Table IV. Polarizabilities and hyperpolarizabilities.

Polarizabilities

Static polarizability

$$\alpha_{ab}(0;0) = -Tr[H^aD^b(0)] \quad \text{(IV-1a)}$$

Dynamic polarizability:

$$\alpha_{ab}(\mp\omega;\pm\omega) = -Tr[H^aD^b(\pm\omega)] \quad \text{(IV-1b)}$$

Hyperpolarizabilities

Static hyperpolarizability

$$\beta_{abc}(0;0,0) = -Tr[H^aD^{bc}(0,0)] \quad \text{(IV-2a)}$$

Electrooptic Pockels effect (EOPE)

$$\beta_{abc}(\mp\omega;0,\pm\omega) = -Tr[H^aD^{bc}(0,\pm\omega)] \quad \text{(IV-2b)}$$

Second harmonic generation (SHG)

$$\beta_{abc}(\mp 2\omega;\pm\omega,\pm\omega) = -Tr[H^aD^{bc}(\pm\omega,\pm\omega)] \quad \text{(IV-2c)}$$

Optical rectification (OR)

$$\beta_{abc}(0;\pm\omega,\mp\omega) = -Tr[H^aD^{bc}(\pm\omega,\mp\omega)] \quad \text{(IV-2d)}$$

Second hyperpolarizabilities

Static second hyperpolarizability

$$\gamma_{abcd}(0;0,0,0) = -Tr[H^aD^{bcd}(0,0,0)] \quad \text{(IV-3a)}$$

Optical Kerr effect (OKE)

$$\gamma_{abcd}(\mp\omega;0,0,\pm\omega) = -\mathrm{Tr}[H^aD^{bcd}(0,0,\pm\omega)] \quad \text{(IV-3b)}$$

DC-electric field induced second harmonic generation (EFISHG)

$$\gamma_{abcd}(\mp 2\omega;0,\pm\omega,\pm\omega) = -Tr[H^aD^{bcd}(0,\pm\omega,\pm\omega)] \quad \text{(IV-3c)}$$

Third harmonic generation (THG)

$$\gamma_{abcd}(\mp 3\omega;\pm\omega,\pm\omega,\pm\omega) = -Tr[H^aD^{bcd}(\pm\omega,\pm\omega,\pm\omega)] \quad \text{(IV-3d)}$$

DC-electric field induced optical rectification (EFIOR)

$$\gamma_{abcd}(0;0,\pm\omega,\mp\omega) = -Tr[H^aD^{bcd}(0,\pm\omega,\mp\omega)] \quad \text{(IV-3e)}$$

Intensity dependent refractive index (IDRI)

$$\gamma_{abcd}(\mp\omega;\pm\omega,\pm\omega,\mp\omega) = -Tr[H^aD^{bcd}(\pm\omega,\pm\omega,\mp\omega)] \quad \text{(IV-3f)}$$

Solution of the First-Order CPHF Equations

Multiplying eq. (I-1a) on the left by $C^{0\dagger}$ and using eqs. (24a), (27a), and (II) together with the relationship

$$C^{0\dagger}F^0C^0 = \varepsilon^0, \quad (33)$$

and rearranging the resulting equation we get

$$\varepsilon^a(\pm\omega) = G^a(\pm\omega) + \varepsilon^0U^a(\pm\omega) - U^a(\pm\omega)\varepsilon^0 \pm \omega U^a(\pm\omega). \quad (34)$$

It should be noted that the Lagrangian multiplier matrix ε is at least block diagonal in all orders. Thus in the first order, for $i \in$ occ; $j \in$ virt, and $i \in$ virt; $j \in$ occ,

$$\varepsilon^a_{ij}(\pm\omega) = 0, \quad (35)$$

where occ and virt represent the occupied and virtual MO's, respectively. Substituting eq. (35) in eq. (34) the occ − virt and virt − occ blocks of $U^a(\pm\omega)$ matrix are given by

$$U^a_{ij}(\pm\omega) = \frac{G^a_{ij}(\pm\omega)}{\varepsilon^0_j - \varepsilon^0_i \mp \omega}. \quad (36)$$

The above equation may be used to calculate the occ − occ and virt − virt blocks of $U^a(\pm\omega)$ matrix, however, this may lead to difficulties in the limit ($\omega \to 0$) if the zeroth order eigenvalues ε^0 have some degeneracies or when ω is equal to an orbital energy transition. This situation can be avoided by choosing a noncanonical solution for the diagonal blocks of the U matrix instead of a canonical solution.[43–45] Accordingly from the first order orthonormalization eq. (II-1a)

$$U^a(\pm\omega) + U^{a\dagger}(\mp\omega) = 0. \quad (37)$$

We choose for the diagonal blocks

$$U^a(\pm\omega) = U^{a\dagger}(\mp\omega), \quad (38)$$

so that from eq. (37)

$$U^a(\pm\omega) = 0. \quad (39)$$

Thus from the choice of the solution, we have made the first-order transformation matrix $U^a(\pm\omega)$ to be block off-diagonal with zero in the diagonal blocks. The corresponding equations for the static case ($\omega = 0$) can be obtained by simply substituting $\omega = 0$ in eqs. (34) through (39). Because of the form of the density matrix (eq. (III-1A)) one needs both $U(+\omega)$ and $U(-\omega)$. This problem is simplified by the use of the orthonormalization equations. Thus for example, once $U(+\omega)$ has been computed, $C(+\omega)$ is computed from eq. (24a) while $C(-\omega)$ can be computed using eq. (37) as

$$C(-\omega) = -C^0U^\dagger(+\omega). \quad (40)$$

This eliminates the need to separately construct and store the $U(-\omega)$matrix.

Solution of the Second-Order CPHF Equations

Second Harmonic Generation (SHG)

Proceeding in the same manner as for the first order, we obtain from eq. (I-2a)

$$\begin{aligned}\varepsilon^{ab}(\pm\omega,\pm\omega) = {} & G^{ab}(\pm\omega,\pm\omega) \\ & + G^a(\pm\omega)U^b(\pm\omega) + G^b(\pm\omega)U^a(\pm\omega) \\ & - U^a(\pm\omega)\varepsilon^b(\pm\omega) - U^b(\pm\omega)\varepsilon^a(\pm\omega) \\ & + \varepsilon^0U^{ab}(\pm\omega,\pm\omega) - U^{ab}(\pm\omega,\pm\omega)\varepsilon^0 \\ & \pm 2\omega U^{ab}(\pm\omega,\pm\omega). \quad (41)\end{aligned}$$

For $i \in$ occ; $j \in$ virt, and $i \in$ virt; $j \in$ occ

$$\varepsilon_{ij}^{ab} = 0, \tag{42}$$

so that the off-diagonal blocks of $U^{ab}(\pm\omega, \pm\omega)$ are given by

$$U_{ij}^{ab}(\pm\omega, \pm\omega) = \frac{G_{ij}^{ab}(\pm\omega, \pm\omega) + T_{ij}^{ab}(\pm\omega, \pm\omega)}{\varepsilon_j^0 - \varepsilon_i^0 \mp 2\varepsilon}, \tag{43}$$

where

$$T_{ij}^{ab}(\pm\omega, \pm\omega) = \sum_k^{\text{all}} (G_{ik}^a(\pm\omega)U_{kj}^b(\pm\omega) + G_{ik}^b(\pm\omega)U_{kj}^a(\pm\omega) - U_{ik}^a(\pm\omega)\varepsilon_{kj}^b(\pm\omega) - U_{ik}^b(\pm\omega)\varepsilon_{kj}^a(\pm\omega)) \tag{44}$$

is the constant part of the U^{ab} matrix coming from the first order solution. In eq. (44) all is occ + virt. Substitution of eq. (34) for $\varepsilon^a(\pm\omega)$ and $\varepsilon^b(\pm\omega)$ into eq. (44) and making use of the fact that for $i \in$ occ; $j \in$ virt and $i \in$ virt; $j \in$ occ

$$\sum_k^{\text{all}} U_{ik}^a(\pm\omega)U_{ik}^b(\pm\omega) = 0, \tag{45}$$

gives

$$T_{ij}^{ab}(\pm\omega, \pm\omega) = \sum_k^{\text{all}} (G_{ik}^a(\pm\omega)U_{kj}^b(\pm\omega) + G_{ik}^b(\pm\omega)U_{kj}^a(\pm\omega) - U_{ik}^a(\pm\omega)G_{kj}^b(\pm\omega) - U_{ik}^b(\pm\omega)G_{kj}^a(\pm\omega)). \tag{46}$$

For the diagonal blocks we use the orthonormalization eq. (II-2a) which can be written as

$$U^{ab}(\pm\omega, \pm\omega) + U^{a\dagger}(\mp\omega)U^b(\pm\omega) + U^{b\dagger}(\mp\omega)U^a(\pm\omega) + U^{ab\dagger}(\mp\omega, \mp\omega) = 0. \tag{47}$$

Here again we make the choice that for the diagonal blocks

$$U^{ab}(\pm\omega, \pm\omega) = U^{ab\dagger}(\mp\omega, \mp\omega), \tag{48}$$

so that the diagonal blocks of $U^{ab}(\pm\omega, \pm\omega)$ are given by

$$U^{ab}(\pm\omega, \pm\omega) = -\tfrac{1}{2}\{U^{a\dagger}(\mp\omega)U^b(\pm\omega) + U^{b\dagger}(\mp\omega)U^a(\pm\omega)\}. \tag{49}$$

Eq. (49) can be further simplified by using eq. (37) as

$$U^{ab}(\pm\omega, \pm\omega) = \tfrac{1}{2}\{U^a(\pm\omega)U^b(\pm\omega) + U^b(\pm\omega)U^a(\pm\omega)\}. \tag{50}$$

Thus the diagonal and the off-diagonal blocks of the $U^{ab}(\pm\omega, \pm\omega)$ matrix are computed from eqs. (50) and (43), respectively. In fact, one only needs to compute $U^{ab}(+\omega, +\omega)$ explicitly while $U^{ab}(-\omega, -\omega)$, which is needed for the construction of the density matrix can then be computed from eq. (47) as

$$U^{ab}(-\omega, -\omega) = W^{ab\dagger}(+\omega, +\omega) - U^{ab\dagger}(+\omega, +\omega), \tag{51}$$

where

$$W^{ab}(+\omega, +\omega) = U^a(+\omega)U^b(+\omega) + U^b(+\omega)U^a(+\omega). \tag{52}$$

Following the same procedure the U matrices for the other second-order terms and also the third-order terms are formed, the final expressions for all terms are given in Tables V and VI, respectively.

NONITERATIVE CALCULATIONS OF HYPERPOLARIZABILITIES

While the iterative calculation of the nonlinear optical effects using the expressions given in the previous section is straightforward, it should be noted that for computations involving βs (four) and γs (six) with each β having six independent components and each γ having 10 independent components in Kleinman symmetry (excluding any other symmetry that may occur), a total of 90 iterative calculations, each equivalent to one SCF calculation is required. On the other hand, the number of iterative calculations reduces to 40 for the same problem if one uses the $(2n + 1)$ rule of the perturbation theory, as will be shown in this section. However, the derivation of appropriate analytical expressions for computing βs and γs using the $(2n + 1)$ rule is rather involved as can be seen from the work of Hurst and Dupuis[21] for the static case. The dynamic cases are even more involved and require several manipulations. For reason of brevity, we describe in this section the various steps involved in the derivation of β(SHG) and then give final expressions for EOPE, OR, and the static hyperpolarizability. A similar approach is taken for the third-order processes where we describe the various steps involved in the derivation of γ(THG) and then give the final expressions for DC-EFISHG, IDRI, OKE, DC-EFIOR, and the static second hyperpolarizability. The detailed mathematical treatment giving step-by-step derivation of the various effects can be found in a technical report.[49]

Hyperpolarizabilities

The following steps are taken to derive the hyperpolarizability expressions which satisfy the $(2n + 1)$ rule.

SHG

Step 1. Start with the second-order CPHF equation for SHG, eq. (I-2a) with positive argument, $(+\omega, +\omega)$ in direction bc and left multiply it with $C^{a\dagger}(+2\omega)$.

Step 2. Take the adjoint of the first-order CPHF equation (I-1a) with argument $(+2\omega)$ and in direction a and right multiply it with $C^{bc}(+\omega, +\omega)$.

Table V. Solution of the first- and second-order CPHF equations.

Polarizabilities

Off-diagonal blocks

$$U^{a}_{ij}(\pm\omega) = \frac{G^{a}_{ij}(\pm\omega)}{\varepsilon^0_j - \varepsilon^0_i \mp \omega}. \tag{V-1a}$$

Diagonal blocks

$$U^{a}(\pm\omega) = 0. \tag{V-1b}$$

Second harmonic generation (SHG)

Off-diagonal blocks

$$U^{ab}_{ij}(\pm\omega, \pm\omega) = \frac{G^{ab}_{ij}(\pm\omega, \pm\omega) + T^{ab}_{ij}(\pm\omega, \pm\omega)}{\varepsilon^0_j - \varepsilon^0_i \mp 2\omega}, \tag{V-2a}$$

$$T^{ab}_{ij}(\pm\omega, \pm\omega) = \sum_k^{\text{all}} (G^{a}_{ik}(\pm\omega)U^{b}_{kj}(\pm\omega) + G^{b}_{ik}(\pm\omega)U^{a}_{kj}(\pm\omega) - U^{a}_{ik}(\pm\omega)\varepsilon^{b}_{kj}(\pm\omega) - U^{b}_{ik}(\pm\omega)\varepsilon^{a}_{kj}(\pm\omega)) \tag{V-2b}$$

Diagonal blocks

$$U^{ab}(\pm\omega, \pm\omega) = \tfrac{1}{2}\{U^{a}(\pm\omega)U^{b}(\pm\omega) + U^{b}(\pm\omega)U^{a}(\pm\omega)\}. \tag{V-2c}$$

$$U^{ab}(-\omega, -\omega) = W^{ab\dagger}(+\omega, +\omega) - U^{ab\dagger}(+\omega, +\omega), \tag{V-2d}$$

$$W^{ab}(+\omega, +\omega) = U^{a}(+\omega)U^{b}(+\omega) + U^{b}(+\omega)U^{a}(+\omega). \tag{V-2e}$$

Electrooptic Pockels effect (EOPE)

Off-diagonal blocks

$$U^{ab}_{ij}(0, \pm\omega) = \frac{G^{ab}_{ij}(0, \pm\omega) + T^{ab}_{ij}(0, \pm\omega)}{\varepsilon^0_j - \varepsilon^0_i \pm \omega}, \tag{V-3a}$$

$$T^{ab}_{ij}(0, \pm\omega) = \sum_k^{\text{all}} (G^{a}_{ik}(0)U^{b}_{kj}(\pm\omega) + G^{b}_{ik}(\pm\omega)U^{a}_{kj}(0) - U^{a}_{ik}(0)G^{b}_{kj}(\pm\omega) - U^{b}_{ik}(\pm\omega)G^{a}_{kj}(0)). \tag{V-3b}$$

Diagonal blocks

$$U^{ab}(0, \pm\omega) = \tfrac{1}{2}\{U^{a}(0)U^{b}(\pm\omega) + U^{b}(\pm\omega)U^{a}(0)\}, \tag{V-3c}$$

$$U^{ab}(0, -\omega) = W^{ab\dagger}(0, +\omega) - U^{ab\dagger}(0, +\omega), \tag{V-3d}$$

$$W^{ab}(0, +\omega) = U^{a}(0)U^{b}(+\omega) + U^{b}(+\omega)U^{a}(0). \tag{V-3e}$$

Optical rectification (OR).

Off-diagonal blocks

$$U^{ab}_{ij}(\pm\omega, \mp\omega) = \frac{G^{ab}_{ij}(\pm\omega, \mp\omega) + T^{ab}_{ij}(\pm\omega, \mp\omega)}{\varepsilon^0_j - \varepsilon^0_i}, \tag{V-4a}$$

$$T^{ab}_{ij}(\pm\omega, \mp\omega) = \sum_k^{\text{all}} (G^{a}_{ik}(\pm\omega)U^{b}_{kj}(\mp\omega) + G^{b}_{ik}(\mp\omega)U^{a}_{kj}(\pm\omega) - U^{a}_{ik}(\pm\omega)G^{b}_{kj}(\mp\omega) - U^{b}_{ik}(\mp)G^{a}_{kj}(\pm\omega)). \tag{V-4b}$$

Table V. (*Continued*)

Diagonal blocks

$$U^{ab}(\pm\omega, \mp\omega) = \tfrac{1}{2}\{U^{a}(\pm\omega)U^{b}(\mp\omega) + U^{b}(\mp\omega)U^{a}(\pm\omega)\}, \tag{V-4c}$$

$$U^{ab}(-\omega, +\omega) = W^{ab\dagger}(+\omega, -\omega) - U^{ab\dagger}(+\omega, -\omega), \tag{V-4d}$$

$$W^{ab}(+\omega, -\omega) = U^{a}(+\omega)U^{b}(-\omega) + U^{b}(-\omega)U^{a}(+\omega). \tag{V-4e}$$

Static hyperpolarizability

Off-diagonal blocks

$$U^{ab}_{ij}(0, 0) = \frac{G^{ab}_{ij}(0, 0) + T^{ab}_{ij}(0, 0)}{\varepsilon^0_j - \varepsilon^0_i}, \tag{V-5a}$$

$$T^{ab}_{ij}(0, 0) = \sum_k^{\text{all}} (G^{a}_{ik}(0)U^{b}_{kj}(0) + G^{b}_{ik}(0)U^{a}_{kj}(0) - U^{a}_{ik}(0)G^{b}_{kj}(0) - U^{b}_{ik}(0)G^{a}_{kj}(0)). \tag{V-5b}$$

Diagonal blocks

$$U^{ab}(0, 0) = \tfrac{1}{2}\{U^{a}(0)U^{b}(0) + U^{b}(0)U^{a}(0)\}. \tag{V-5c}$$

Step 3. Subtract the equation resulting from Step 2 from that resulting from Step 1.

Step 4. Take the adjoint of the second order equation (I-2a) with argument $(-\omega, -\omega)$ and in direction bc and right multiply it with $C^{a}(-2\omega)$.

Step 5. Take the first-order equation (I-1a) with argument (-2ω) and left multiply it with $C^{bc\dagger}(-\omega, -\omega)$.

Step 6. Subtract the equation resulting from Step 5 from that resulting from Step 4.

Step 7. Add the equations resulting in Step 3 and Step 6.

At this point it is necessary to eliminate some second-order terms, for example C^{bc} and ε^{bc}, by using the first-order normalization conditions and rewriting the equation in terms of the expression for the density matrix $D^{bc}(+\omega, +\omega)$ and the first-order one electron Hamiltonian matrix, $H^{a}(+\omega)$. The required manipulations are described in the following step.

Step 8. Multiply the equation obtained in Step 7 by the occupation number matrix n, take the trace (Tr), and add the quantity

$$Tr[n\{C^{b\dagger}(-\omega)F^{a}(-2\omega)C^{c}(+\omega) + C^{c\dagger}(-\omega)F^{a\dagger}(+2\omega)C^{b}(+\omega)\}],$$

to both sides of the resulting equation. Here, one uses the facts that $\varepsilon^0 = \varepsilon^{0\dagger}$, $\varepsilon^{a}(+\omega) = \varepsilon^{a}(-\omega)^\dagger$, $\varepsilon^{bc}(+\omega, +\omega) = \varepsilon^{bc}(-\omega, -\omega)^\dagger$, and that $n\varepsilon^0 = \varepsilon^0 n$, $n\varepsilon^a = \varepsilon^a n$, $n\varepsilon^{ab} = \varepsilon^{ab}n, \ldots$. Then, after permutation of the matrices as shown in Appendix B and rearranging the

Table VI. Solution of the third-order CPHF equations.

Third harmonic generation (THG)

Off-diagonal blocks

$$U_{ij}^{abc}(\pm\omega, \pm\omega, \pm\omega) = \frac{G_{ij}^{abc}(\pm\omega, \pm\omega, \pm\omega) + T_{ij}^{abc}(\pm\omega, \pm\omega, \pm\omega)}{\varepsilon_j^0 - \varepsilon_i^0 \mp 3\omega}, \tag{VI-1a}$$

$$\begin{aligned} T_{ij}^{abc}(\pm\omega, \pm\omega, \pm\omega) = \sum_k^{\text{all}} \big(& G_{ik}^{a}(\pm\omega)U_{kj}^{bc}(\pm\omega, \pm\omega) + G_{ik}^{bc}(\pm\omega, \pm\omega)U_{kj}^{a}(\pm\omega) - U_{ik}^{a}(\pm\omega)\varepsilon_{kj}^{bc}(\pm\omega, \pm\omega) \\ & - U_{ik}^{bc}(\pm\omega, \pm\omega)\varepsilon_{kj}^{a}(\pm\omega) + G_{ik}^{b}(\pm\omega)U_{kj}^{ac}(\pm\omega, \pm\omega) + G_{ik}^{ac}(\pm\omega, \pm\omega)U_{kj}^{b}(\pm\omega) \\ & - U_{ik}^{b}(\pm\omega)\varepsilon_{kj}^{ac}(\pm\omega, \pm\omega) - U_{ik}^{ac}(\pm\omega, \pm\omega)\varepsilon_{kj}^{b}(\pm\omega) + G_{ik}^{c}(\pm\omega)U_{kj}^{ab}(\pm\omega, \pm\omega) \\ & + G_{ik}^{ab}(\pm\omega, \pm\omega)U_{kj}^{c}(\pm\omega) - U_{ik}^{c}(\pm\omega)\varepsilon_{kj}^{ab}(\pm\omega, \pm\omega) - U_{ik}^{ab}(\pm\omega, \pm\omega)\varepsilon_{kj}^{c}(\pm\omega)\big). \end{aligned} \tag{VI-1b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(\pm\omega, \pm\omega, \pm\omega) = \tfrac{1}{2}\{& U^{a}(\pm\omega)U^{bc}(\pm\omega, \pm\omega) - U^{bc\dagger}(\mp\omega, \mp\omega)U^{a}(\pm\omega) + U^{b}(\pm\omega)U^{ac}(\pm\omega, \pm\omega) \\ & - U^{ac\dagger}(\mp\omega, \mp\omega)U^{b}(\pm\omega) + U^{c}(\pm\omega)U^{ab}(\pm\omega, \pm\omega) - U^{ab\dagger}(\mp\omega, \mp\omega)U^{c}(\pm\omega)\}, \end{aligned} \tag{VI-1c}$$

$$U^{abc}(-\omega, -\omega, -\omega) = W^{abc\dagger}(+\omega, +\omega, +\omega) - U^{abc\dagger}(+\omega, +\omega, +\omega), \tag{VI-1d}$$

$$\begin{aligned} W^{abc}(+\omega, +\omega, +\omega) = {}& U^{a}(+\omega)U^{bc}(+\omega, +\omega) - U^{bc\dagger}(-\omega, -\omega)U^{a}(+\omega) + U^{b}(+\omega)U^{ac}(+\omega, +\omega) \\ & - U^{ac\dagger}(-\omega, -\omega)U^{b}(+\omega) + U^{c}(+\omega)U^{ab}(+\omega, +\omega) - U^{ab\dagger}(-\omega, -\omega)U^{c}(+\omega). \end{aligned} \tag{VI-1e}$$

DC-electric field induced second harmonic generation (EFISHG)

Off-diagonal blocks

$$U_{ij}^{abc}(0, \pm\omega, \pm\omega) = \frac{G_{ij}^{abc}(0, \pm\omega, \pm\omega) + T_{ij}^{abc}(0, \pm\omega, \pm\omega)}{\varepsilon_j^0 - \varepsilon_i^0 \mp 2\omega}, \tag{VI-2a}$$

$$\begin{aligned} T_{ij}^{abc}(0, \pm\omega, \pm\omega) = \sum_k^{\text{all}} \big(& G_{ik}^{a}(0)U_{kj}^{bc}(\pm\omega, \pm\omega) + G_{ik}^{bc}(\pm\omega, \pm\omega)U_{kj}^{a}(0) - U_{ik}^{a}(0)\varepsilon_{kj}^{bc}(\pm\omega, \pm\omega) \\ & - U_{ik}^{bc}(\pm\omega, \pm\omega)\varepsilon_{kj}^{a}(0) + G_{ik}^{b}(\pm\omega)U_{kj}^{ac}(0, \pm\omega) + G_{ik}^{ac}(0, \pm\omega)U_{kj}^{b}(\pm\omega) \\ & - U_{ik}^{b}(\pm\omega)\varepsilon_{kj}^{ac}(0, \pm\omega) - U_{ik}^{ac}(0, \pm\omega)\varepsilon_{kj}^{b}(\pm\omega) + G_{ik}^{c}(\pm\omega)U_{kj}^{ab}(0, \pm\omega) \\ & + G_{ik}^{ab}(0, \pm\omega)U_{kj}^{c}(\pm\omega) - U_{ik}^{c}(\pm\omega)\varepsilon_{kj}^{ab}(0, \pm\omega) - U_{ik}^{ab}(0, \pm\omega)\varepsilon_{kj}^{c}(\pm\omega)\big). \end{aligned} \tag{VI-2b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(0, \pm\omega, \pm\omega) = \tfrac{1}{2}\{& U^{a}(0)U^{bc}(\pm\omega, \pm\omega) - U^{bc\dagger}(\mp\omega, \mp\omega)U^{a}(0) + U^{b}(\pm\omega)U^{ac}(0, \pm\omega) \\ & - U^{ac\dagger}(0, \mp\omega)U^{b}(\pm\omega) + U^{c}(\pm\omega)U^{ab}(0, \pm\omega) - U^{ab\dagger}(0, \mp\omega)U^{c}(\pm\omega)\}, \end{aligned} \tag{VI-2c}$$

$$U^{abc}(0, -\omega, -\omega) = W^{abc\dagger}(0, +\omega, +\omega) - U^{abc\dagger}(0, +\omega, +\omega), \tag{VI-2d}$$

$$\begin{aligned} W^{abc}(0, +\omega, +\omega) = {}& U^{a}(0)U^{bc}(+\omega, +\omega) - U^{bc\dagger}(-\omega, -\omega)U^{a}(0) + U^{b}(+\omega)U^{ac}(0, +\omega) \\ & - U^{ac\dagger}(0, -\omega)U^{b}(+\omega) + U^{c}(+\omega)U^{ab}(0, +\omega) - U^{ab\dagger}(0, -\omega)U^{c}(+\omega). \end{aligned} \tag{VI-2e}$$

Intensity dependent refractive index (IDRI)

Off-diagonal blocks

$$U_{ij}^{abc}(\pm\omega, \pm\omega, \mp\omega) = \frac{G_{ij}^{abc}(\pm\omega, \pm\omega, \mp\omega) + T_{ij}^{abc}(\pm\omega, \pm\omega, \mp\omega)}{\varepsilon_j^0 - \varepsilon_i^0 \mp \omega}, \tag{VI-3a}$$

$$\begin{aligned} T_{ij}^{abc}(\pm\omega, \pm\omega, \mp\omega) = \sum_k^{\text{all}} \big(& G_{ik}^{a}(\pm\omega)U_{kj}^{bc}(\pm\omega, \mp\omega) + G_{ik}^{bc}(\pm\omega, \mp\omega)U_{kj}^{a}(\pm\omega) - U_{ik}^{a}(\pm\omega)\varepsilon_{kj}^{bc}(\pm\omega, \mp\omega) \\ & - U_{ik}^{bc}(\pm\omega, \mp\omega)\varepsilon_{kj}^{a}(\pm\omega) + G_{ik}^{b}(\pm\omega)U_{kj}^{ac}(\pm\omega, \mp\omega) + G_{ik}^{ac}(\pm\omega, \mp\omega)U_{kj}^{b}(\pm\omega) \\ & - U_{ik}^{b}(\pm\omega)\varepsilon_{kj}^{ac}(\pm\omega, \mp\omega) - U_{ik}^{ac}(\pm\omega, \mp\omega)\varepsilon_{kj}^{b}(\pm\omega) + G_{ik}^{c}(\mp\omega)U_{kj}^{ab}(\pm\omega, \pm\omega) \\ & + G_{ik}^{ab}(\pm\omega, \pm\omega)U_{kj}^{c}(\mp\omega) - U_{ik}^{c}(\mp\omega)\varepsilon_{kj}^{ab}(\pm\omega, \pm\omega) - U_{ik}^{ab}(\pm\omega, \pm\omega)\varepsilon_{kj}^{c}(\mp\omega)\big). \end{aligned} \tag{VI-3b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(\pm\omega, \pm\omega, \mp\omega) = \tfrac{1}{2}\{& U^{a}(\pm\omega)U^{bc}(\pm\omega, \mp\omega) - U^{bc\dagger}(\mp\omega, \pm\omega)U^{a}(\pm\omega) + U^{b}(\pm\omega)U^{ac}(\pm\omega, \mp\omega) \\ & - U^{ac\dagger}(\mp\omega, \pm\omega)U^{b}(\pm\omega) - U^{c\dagger}(\pm\omega)U^{ab}(\pm\omega, \pm\omega) - U^{ab\dagger}(\mp\omega, \mp\omega)U^{c\dagger}(\pm\omega)\}, \end{aligned} \tag{VI-3c}$$

$$U^{abc}(-\omega, -\omega, +\omega) = W^{abc\dagger}(+\omega, +\omega, -\omega) - U^{abc\dagger}(+\omega, +\omega, -\omega), \tag{VI-3d}$$

$$\begin{aligned} W^{abc}(+\omega, +\omega, -\omega) = {}& U^{a}(+\omega)U^{bc}(+\omega, -\omega) - U^{bc\dagger}(-\omega, +\omega)U^{a}(+\omega) + U^{b}(+\omega)U^{ac}(+\omega, -\omega) \\ & - U^{ac\dagger}(-\omega, +\omega)U^{b}(+\omega) - U^{c\dagger}(+\omega)U^{ab}(+\omega, +\omega) - U^{ab\dagger}(-\omega, -\omega)U^{c\dagger}(+\omega). \end{aligned} \tag{VI-3e}$$

Table VI. *(Continued)*

Optical Kerr effect (OKE)

Off-diagonal blocks

$$U_{ij}^{abc}(0, 0, \pm\omega) = \frac{G_{ij}^{abc}(0, 0, \pm\omega) + T_{ij}^{abc}(0, 0, \pm\omega)}{\varepsilon_j^0 - \varepsilon_i^0 \mp \omega}, \tag{VI-4a}$$

$$\begin{aligned} T_{ij}^{abc}(0, 0, \pm\omega) = \sum_k^{\text{all}} \big(&G_{ik}^a(0)U_{kj}^{bc}(0, \pm\omega) + G_{ik}^{bc}(0, \pm\omega)U_{kj}^a(0) - U_{ik}^a(0)\varepsilon_{kj}^{bc}(0, \pm\omega) \\ &- U_{ik}^{bc}(0, \pm\omega)\varepsilon_{kj}^a(0) + G_{ik}^b(0)U_{kj}^{ac}(0, \pm\omega) + G_{ik}^{ac}(0, \pm\omega)U_{kj}^b(0) \\ &- U_{ik}^b(0)\varepsilon_{kj}^{ac}(0, \pm\omega) - U_{ik}^{ac}(0, \pm\omega)\varepsilon_{kj}^b(0) + G_{ik}^c(\pm\omega)U_{kj}^{ab}(0, 0) \\ &+ G_{ik}^{ab}(0, 0)U_{kj}^c(\pm\omega) - U_{ik}^c(\pm\omega)\varepsilon_{kj}^{ab}(0, 0) - U_{ik}^{ab}(0, 0)\varepsilon_{kj}^c(\pm\omega)\big). \end{aligned} \tag{VI-4b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(0, 0, \pm\omega) = \tfrac{1}{2}\{&U^a(0)U^{bc}(0, \pm\omega) - U^{bc\dagger}(0, \mp\omega)U^a(0) + U^b(0)U^{ac}(0, \pm\omega) \\ &- U^{ac\dagger}(0, \mp\omega)U^b(0) + U^c(\pm\omega)U^{ab}(0, 0) - U^{ab\dagger}(0, 0)U^c(\pm\omega)\}, \end{aligned} \tag{VI-4c}$$

$$U^{abc}(0, 0, -\omega) = W^{abc\dagger}(0, 0, +\omega) - U^{abc\dagger}(0, 0, +\omega), \tag{VI-4d}$$

$$\begin{aligned} W^{abc}(0, 0, +\omega) = &U^a(0)U^{bc}(0, +\omega) - U^{bc\dagger}(0, -\omega)U^a(0) + U^b(0)U^{ac}(0, +\omega) \\ &- U^{ac\dagger}(0, -\omega)U^b(0) + U^c(+\omega)U^{ab}(0, 0) - U^{ab\dagger}(0, 0)U^c(+\omega). \end{aligned} \tag{VI-4e}$$

DC-electric field induced optical rectification (EFIOR)

Off-diagonal blocks

$$U_{ij}^{abc}(0, \pm\omega, \mp\omega) = \frac{G_{ij}^{abc}(0, \pm\omega, \mp\omega) + T_{ij}^{abc}(0, \pm\omega, \mp\omega)}{\varepsilon_j^0 - \varepsilon_i^0}, \tag{VI-5a}$$

$$\begin{aligned} T_{ij}^{abc}(0, \pm\omega, \mp\omega) = \sum_k^{\text{all}} \big(&G_{ik}^a(0)U_{kj}^{bc}(\pm\omega, \mp\omega) + G_{ik}^{bc}(\pm\omega, \mp\omega)U_{kj}^a(0) - U_{ik}^a(0)\varepsilon_{kj}^{bc}(\pm\omega, \mp\omega) \\ &- U_{ik}^{bc}(\pm\omega, \mp\omega)\varepsilon_{kj}^a(0) + G_{ik}^b(\pm\omega)U_{kj}^{ac}(0, \mp\omega) + G_{ik}^{ac}(0, \mp\omega)U_{kj}^b(\pm\omega) \\ &- U_{ik}^b(\pm\omega)\varepsilon_{kj}^{ac}(0, \mp\omega) - U_{ik}^{ac}(0, \mp\omega)\varepsilon_{kj}^b(\pm\omega) + G_{ik}^c(\mp\omega)U_{kj}^{ab}(0, \pm\omega) \\ &+ G_{ik}^{ab}(0, \pm\omega)U_{kj}^c(\mp\omega) - U_{ik}^c(\mp\omega)\varepsilon_{kj}^{ab}(0, \pm\omega) - U_{ik}^{ab}(0, \pm\omega)\varepsilon_{kj}^c(\mp\omega)\big). \end{aligned} \tag{VI-5b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(0, \pm\omega, \mp\omega) = \tfrac{1}{2}\{&U^a(\pm\omega)U^{bc}(\pm\omega, \mp\omega) - U^{bc\dagger}(\mp\omega, \pm\omega)U^a(0) + U^b(\pm\omega)U^{ac}(0, \mp\omega) \\ &- U^{ac\dagger}(0, \pm\omega)U^b(\pm\omega) - U^{c\dagger}(\pm\omega)U^{ab}(0, \pm\omega) - U^{ab\dagger}(0, \mp\omega)U^{c\dagger}(\pm\omega)\}. \end{aligned} \tag{VI-5c}$$

$$U^{abc}(0, -\omega, +\omega) = W^{abc\dagger}(0, +\omega, -\omega) - U^{abc\dagger}(0, +\omega, -\omega), \tag{VI-5d}$$

$$\begin{aligned} W^{abc}(0, +\omega, -\omega) = &U^a(0)U^{bc}(+\omega, -\omega) - U^{bc\dagger}(-\omega, +\omega)U^a(0) + U^b(+\omega)U^{ac}(0, -\omega) \\ &- U^{ac\dagger}(0, +\omega)U^b(+\omega) - U^{c\dagger}(+\omega)U^{ab}(0, +\omega) - U^{ab\dagger}(0, -\omega)U^{c\dagger}(+\omega). \end{aligned} \tag{VI-5e}$$

Static second hyperpolarizability

Off-diagonal blocks

$$U_{ij}^{abc}(0, 0, 0) = \frac{G_{ij}^{abc}(0, 0, 0) + T_{ij}^{abc}(0, 0, 0)}{\varepsilon_j^0 - \varepsilon_i^0}, \tag{VI-6a}$$

$$\begin{aligned} T_{ij}^{abc}(0, 0, 0) = \sum_k^{\text{all}} \big(&G_{ik}^a(0)U_{kj}^{bc}(0, 0) + G_{ik}^{bc}(0, 0)U_{kj}^a(0) - U_{ik}^a(0)\varepsilon_{kj}^{bc}(0, 0) \\ &- U_{ik}^{bc}(0, 0)\varepsilon_{kj}^a(0) + G_{ik}^b(0)U_{kj}^{ac}(0, 0) + G_{ik}^{ac}(0, 0)U_{kj}^b(0) \\ &- U_{ik}^b(0)\varepsilon_{kj}^{ac}(0, 0) - U_{ik}^{ac}(0, 0)\varepsilon_{kj}^b(0) + G_{ik}^c(0)U_{kj}^{ab}(0, 0) \\ &+ G_{ik}^{ab}(0, 0)U_{kj}^c(0) - U_{ik}^c(0)\varepsilon_{kj}^{ab}(0, 0) - U_{ik}^{ab}(0, 0)\varepsilon_{kj}^c(0)\big), \end{aligned} \tag{VI-6b}$$

Diagonal blocks

$$\begin{aligned} U^{abc}(0, 0, 0) = \tfrac{1}{2}\{&U^a(0)U^{bc}(0, 0) - U^{bc\dagger}(0, 0)U^a(0) + U^b(0)U^{ac}(0, 0) \\ &- U^{ac\dagger}(0, 0)U^b(0) + U^c(0)U^{ab}(0, 0) - U^{ab\dagger}(0, 0)U^c(0)\}. \end{aligned} \tag{VI-6c}$$

resulting equations slightly one obtains the following expression

$$\begin{aligned} &Tr[H^aD^{bc}(+\omega, +\omega)] \\ &= Tr[n\{C^{a\dagger}(+2\omega)F^b(+\omega)C^c(+\omega) \\ &\quad + C^{c\dagger}(-\omega)F^{b\dagger}(-\omega)C^a(-2\omega) \\ &\quad + C^{b\dagger}(-\omega)F^c(+\omega)C^a(-2\omega) \\ &\quad + C^{a\dagger}(+2\omega)F^{c\dagger}(-\omega)C^b(+\omega) \\ &\quad + C^{c\dagger}(-\omega)F^a(-2\omega)C^b(+\omega) \\ &\quad + C^{b\dagger}(-\omega)F^{a\dagger}(+2\omega)C^c(+\omega) \\ &\quad - C^{a\dagger}(+2\omega)S^0C^b(+\omega)\varepsilon^c(+\omega) \\ &\quad - \varepsilon^{c\dagger}(-\omega)C^{b\dagger}(-\omega)S^0C^a(-2\omega) \\ &\quad - C^{a\dagger}(+2\omega)S^0C^c(+\omega)\varepsilon^b(+\omega) \\ &\quad - \varepsilon^{b\dagger}(-\omega)C^{c\dagger}(-\omega)S^0C^a(-2\omega) \\ &\quad - C^{b\dagger}(-\omega)S^0C^c(+\omega)\varepsilon^a(-2\omega) \\ &\quad - \varepsilon^{a\dagger}(+2\omega)C^{c\dagger}(-\omega)S^0C^b(+\omega)\}]. \end{aligned} \tag{53}$$

Substituting the above equation in eq. (IV-2c) and further rearranging the right-hand side one obtains

$$\begin{aligned}
\beta_{abc}(-2\omega;\, +\omega,\, +\omega) = & -Tr[n\{C^{a\dagger}(+2\omega)F^{b}(+\omega)C^{b}(+\omega) \\
& + C^{c\dagger}(-\omega)F^{b\dagger}(-\omega)C^{a}(-2\omega) \\
& + C^{b\dagger}(-\omega)F^{c}(+\omega)C^{a}(-2\omega) \\
& + C^{a\dagger}(+2\omega)F^{c\dagger}(-\omega)C^{b}(+\omega) \\
& + C^{c\dagger}(-\omega)F^{a}(-2\omega)C^{b}(+\omega) \\
& + C^{b\dagger}(-\omega)F^{a\dagger}(+2\omega)C^{c}(+\omega) \\
& - C^{a\dagger}(+2\omega)S^{0}C^{c}(+\omega)\varepsilon^{b}(+\omega) \\
& - \varepsilon^{b\dagger}(-\omega)C^{c\dagger}(-\omega)S^{0}C^{a}(-2\omega) \\
& - C^{b\dagger}(-\omega)S^{0}C^{a}(-2\omega)\varepsilon^{c\dagger}(-\omega) \\
& - \varepsilon^{c}(+\omega)C^{a\dagger}(+2\omega)S^{0}C^{b}(+\omega) \\
& - C^{c\dagger}(-\omega)S^{0}C^{b}(+\omega)\varepsilon^{a\dagger}(+2\omega) \\
& - \varepsilon^{a}(-2\omega)C^{b\dagger}(-\omega)S^{0}C^{c}(+\omega)\}].
\end{aligned} \tag{54}$$

Thus the hyperpolarizability for SHG is obtained in terms of the solution of the first-order CPHF equation without explicitly solving the corresponding second-order equation. For futher simplification, it is convenient to write the right hand side of eq. (54) in molecular-orbital basis terms. Using the definitions of eqs. (24a) and (27a) and making use of the equations given in Table II and (37), one obtains for SHG

$$\begin{aligned}
\beta_{abc}(-2\omega;\, +\omega,\, +\omega) = & \; Tr[n\{U^{a}(-2\omega)G^{b}(+\omega)U^{c}(+\omega) \\
& + U^{c}(+\omega)G^{b}(+\omega)U^{a}(-2\omega) \\
& + U^{b}(+\omega)G^{c}(+\omega)U^{a}(-2\omega) \\
& + U^{a}(-2\omega)G^{c}(+\omega)U^{b}(+\omega) \\
& + U^{c}(+\omega)G^{a}(-2\omega)U^{b}(+\omega) \\
& + U^{b}(+\omega)G^{a}(-2\omega)U^{c}(+\omega)\}] \\
& - Tr[n\{U^{a}(-2\omega)U^{c}(+\omega)\varepsilon^{b}(+\omega) \\
& + U^{c}(+\omega)U^{a}(-2\omega)\varepsilon^{b}(+\omega) \\
& + U^{b}(+\omega)U^{a}(-2\omega)\varepsilon^{c}(+\omega) \\
& + U^{a}(-2\omega)U^{b}(+\omega)\varepsilon^{c}(+\omega) \\
& + U^{c}(+\omega)U^{b}(+\omega)\varepsilon^{a}(-2\omega) \\
& + U^{b}(+\omega)U^{c}(+\omega)\varepsilon^{a}(-2\omega)\}].
\end{aligned} \tag{55}$$

The actual computation of these two type of terms are detailed in Appendix C. The corresponding expressions for hyperpolarizabilities for EOPE, OR and the static case are given in Table VII, and were obtained by following the same Step 1 to Step 8 with the appropriate first and second order equations and coefficient matrices. The equation for the static hyperpolarizability is equivalent to the corresponding equation derived by Hurse and Dupuis.[41]

Second Hyperpolarizabilities

The derivation of the second hyperpolarizabilities follow the same Steps 1 to 8 as described for the hyperpolarizability, but now the second-order CPHF equations and coefficients matrices are replaced by the corresponding third-order quantities. The steps for the THG process are described below.

THG

Step 1. Start with eq. (I-3a) with positive arguments $(+\omega, +\omega, +\omega)$ and in direction *bcd* and left multiply it with $C^{a\dagger}(+3\omega)$.

Table VII. First hyperpolarizabilities.

SHG

$$\begin{aligned}
\beta_{abc}(-2\omega;\, +\omega,\, +\omega) = & \; Tr[n\{U^{a}(-2\omega)G^{b}(+\omega)U^{c}(+\omega) + U^{c}(+\omega)G^{b}(+\omega)U^{a}(-2\omega) + U^{b}(+\omega)G^{c}(+\omega)U^{a}(-2\omega) \\
& + U^{a}(-2\omega)G^{c}(+\omega)U^{b}(+\omega) + U^{c}(+\omega)G^{a}(-2\omega)U^{b}(+\omega) + U^{b}(+\omega)G^{a}(-2\omega)U^{c}(+\omega)\}] \\
& - Tr[n\{U^{a}(-2\omega)U^{c}(+\omega)\varepsilon^{b}(+\omega) + U^{c}(+\omega)U^{a}(-2\omega)\varepsilon^{b}(+\omega) + U^{b}(+\omega)U^{a}(-2\omega)\varepsilon^{c}(+\omega) \\
& + U^{a}(-2\omega)U^{b}(+\omega)\varepsilon^{c}(+\omega) + U^{c}(+\omega)U^{b}(+\omega)\varepsilon^{a}(-2\omega) + U^{b}(+\omega)U^{c}(+\omega)\varepsilon^{a}(-2\omega)\}].
\end{aligned} \tag{VII-1}$$

EOPE

$$\begin{aligned}
\beta_{abc}(-\omega;\, 0,\, +\omega) = & \; Tr[n\{U^{a}(-\omega)G^{b}(0)U^{c}(+\omega) + U^{c}(+\omega)G^{b}(0)U^{a}(-\omega) + U^{b}(0)G^{c}(+\omega)U^{a}(-\omega) \\
& + U^{a}(-\omega)G^{c}(+\omega)U^{b}(0) + U^{c}(+\omega)G^{a}(-\omega)U^{b}(0) + U^{b}(0)G^{a}(-\omega)U^{c}(+\omega)\}] \\
& - Tr[n\{U^{a}(-\omega)U^{c}(+\omega)\varepsilon^{b}(0) + U^{c}(+\omega)U^{a}(-\omega)\varepsilon^{b}(0) + U^{b}(0)U^{a}(-\omega)\varepsilon^{c}(+\omega) \\
& + U^{a}(-\omega)U^{b}(0)\varepsilon^{c}(+\omega) + U^{c}(+\omega)U^{b}(0)\varepsilon^{a}(-\omega) + U^{b}(0)U^{c}(+\omega)\varepsilon^{a}(-\omega)\}].
\end{aligned} \tag{VII-2}$$

OKE

$$\begin{aligned}
\beta_{abc}(0;\, +\omega,\, -\omega) = & \; Tr[n\{U^{a}(0)G^{b}(+\omega)U^{c}(-\omega) + U^{c}(-\omega)G^{b}(+\omega)U^{a}(0) + U^{b}(+\omega)G^{c}(-\omega)U^{a}(0) \\
& + U^{a}(0)G^{c}(-\omega)U^{b}(+\omega) + U^{c}(-\omega)G^{a}(0)U^{b}(+\omega) + U^{b}(+\omega)G^{a}(0)U^{c}(-\omega)\}] \\
& - Tr[n\{U^{a}(0)U^{c}(-\omega)\varepsilon^{b}(+\omega) + U^{c}(-\omega)U^{a}(0)\varepsilon^{b}(+\omega) + U^{b}(+\omega)U^{a}(0)\varepsilon^{c}(-\omega) \\
& + U^{a}(0)U^{b}(+\omega)\varepsilon^{c}(-\omega) + U^{c}(-\omega)U^{b}(+\omega)\varepsilon^{a}(0) + U^{b}(+\omega)U^{c}(-\omega)\varepsilon^{a}(0)\}].
\end{aligned} \tag{VII-3}$$

Static hyperpolarizability

$$\begin{aligned}
\beta_{abc}(0;\, 0,\, 0) = & \; Tr[n\{U^{a}(0)G^{b}(0)U^{c}(0) + U^{c}(0)G^{b}(0)U^{a}(0) + U^{b}(0)G^{c}(0)U^{a}(0) \\
& + U^{a}(0)G^{c}(0)U^{b}(0) + U^{c}(0)G^{a}(0)U^{b}(0) + U^{b}(0)G^{a}(0)U^{c}(0)\}] \\
& - Tr[n\{U^{a}(0)U^{c}(0)\varepsilon^{b}(0) + U^{c}(0)U^{a}(0)\varepsilon^{b}(0) + U^{b}(0)U^{a}(0)\varepsilon^{c}(0) \\
& + U^{a}(0)U^{b}(0)\varepsilon^{c}(0) + U^{c}(0)U^{b}(0)\varepsilon^{a}(0) + U^{b}(0)U^{c}(0)\varepsilon^{a}(0)\}].
\end{aligned} \tag{VII-4}$$

Step 2. Take the adjoint of the first-order equation (I-1a) with argument $(+3\omega)$ and right multiply it with $C^{bcd}(+\omega, +\omega, +\omega)$.
Step 3. Subtract the equation resulting from Step 1 from that resulting from Step 2.
Step 4. Next, start with the adjoint of the third order equation (I-3a) with the negative argument $(-\omega, -\omega, -\omega)$ and in direction *bcd* and right multiply it with $C^{a}(-3\omega)$.
Step 5. Take the first-order equation (I-1a) with argument (-3ω) in the direction *a* and left multiply it with $C^{bcd\dagger}(-\omega, -\omega, -\omega)$.
Step 6. Subtract the equation obtained in Step 5 from that obtained in Step 4.
Step 7. Add the equations obtained in Step 3 and Step 6.
Step 8. Multiply the equation obtained in Step 7 by the occupation number matrix n, take the trace, and add to both sides of the resulting equation the quantity

$$\begin{aligned}Tr[n\{&C^{b\dagger}(-\omega)F^{a}(-3\omega)C^{cd}(+\omega, +\omega)\\ &+ C^{cd\dagger}(-\omega, -\omega)F^{a}(-3\omega)C^{b}(+\omega)\\ &+ C^{c\dagger}(-\omega)F^{a}(-3\omega)C^{bd}(+\omega, +\omega)\\ &+ C^{bd\dagger}(-\omega, -\omega)F^{a}(-3\omega)C^{c}(+\omega)\\ &+ C^{d\dagger}(-\omega)F^{a}(-3\omega)C^{bc}(+\omega, +\omega)\\ &+ C^{bc\dagger}(-\omega, -\omega)F^{a}(-3\omega)C^{d}(+\omega)\}].\end{aligned}$$

At this point the terms containing ε^0 and ε^{bcd} vanish. The resulting expression, after slight rearrangement and using the definitions of the first- and third-order density matrices is shown in Table VIII (eq. (VI-1a)). Substituting eq. (VIII-1a) in eq. (IV-3d) and using the definitions given in eqs. (24a), (25a), (27a), (28a), and eq. (II) one obtains for THG the expression (VIII-1b) in Table VIII. Thus the second hyperpolarizability for the THG can be (simply) obtained in terms of the first- and second-order solution of the CPHF equations. The right-hand side of eq. (VIII-1b) can be further simplified by using eq. (37), as shown in (VIII-1c). The actual computation of these terms proceeds as described in Appendix C. The expressions for the second hyperpolarizabilities for DC-EFISHG, IDRI, OKE, DC-EFIOR and for the static case are obtained following the similar steps as for THG and are shown in Table VIII. Note that expression (VIII-6) is equivalent the one given by Hurst and Dupuis[41] for the static second hyperpolarizability.

COMPUTATIONAL STRATEGY

A computer program based upon the expressions developed in the previous section to calculate polarizability and hyperpolarizability has been written and is implemented in the ab initio quantum chemistry program package HONDO.[46-48] The different steps in the program are as follows:

Iterative Calculations

C^0 and μ

The zeroth order coefficient matrix are obtained from the standard SCF calculation and stored. The three components of the dipole moment matrix are calculated and stored.

α

To calculate the polarizability,

1. An initial guess for the Fock matrix F^a is made as
$$F^a = \mu^a.$$
2. The G^a, U^a, C^a, and D^a matrices are computed from eqs. (27), (33), (24), and (III-1a, b).
3. The new F^a matrix is computed from eq. (21).
4. At this point convergence test of the elements of the U^a matrix is checked against a threshold value.

Steps 2 to 4 are repeated until convergence is reached. The *ab* element of the α tensor is calculated using eq. (IV-1a) or eq. (IV-1b). At this point U^a and G^a matrices are stored for the β and γ calculation and D^a matrices are stored for a restart or initial guess for future α calculation, at a different frequency, for example.

β

Here the first-order part of D^{bc} and U^{bc} matrices are computed. Taking this constant part of D^{bc} as the initial guess, F^{bc} is calculated from eq. (22). Then steps similar to 2 to 4 of the α calculation are repeated until convergence with respect to the elements of the U^{bc} matrix has been achieved.

The *abc* component of β is calculated for example, for SHG from eq. (IV-2c). At this point the ε^{bc} is also computed and together with the U^{bc}, G^{bc}, and D^{bc} is stored for the calculation of γ and future restart calculation. These steps have to be carried out for each of the four second order effects as given in eqs. (IV-2a, b, c, d).

γ

The calculation of the six different γs follows exactly the same steps as the βs. Here the constant parts of the D^{bcd} and U^{bcd} are computed and with the constant part as the initial guess for the density matrix the F^{abc} matrix is calculated from eq. (23). Then, steps similar to 2 to 4 of the α calculation are repeated until the convergence of the elements of U^{bcd} matrix

Table VIII. Second hyperpolarizabilities.

THG

$$\begin{aligned}
&Tr[H^aD^{bcd}(-3\omega,+\omega,+\omega)]\\
&\quad= Tr[n\{C^{a\dagger}(+3\omega)F^b(+\omega)C^{cd}(+\omega,+\omega) + C^{cd\dagger}(-\omega,-\omega)F^{b\dagger}(-\omega)C^a(-3\omega) + C^{a\dagger}(+3\omega)F^c(+\omega)C^{bd}(+\omega,+\omega)\\
&\qquad + C^{bd\dagger}(-\omega,-\omega)F^{c\dagger}(-\omega)C^a(-3\omega) + C^{a\dagger}(+3\omega)F^d(+\omega)C^{bc}(+\omega,+\omega) + C^{bc\dagger}(-\omega,-\omega)F^{d\dagger}(-\omega)C^a(-3\omega)\\
&\qquad + C^{a\dagger}(+3\omega)F^{cd}(+\omega,+\omega)C^b(+\omega) + C^{b\dagger}(-\omega)F^{cd\dagger}(-\omega,-\omega)C^a(-3\omega) + C^{a\dagger}(+3\omega)F^{bd}(+\omega,+\omega)C^c(+\omega)\\
&\qquad + C^{c\dagger}(-\omega)F^{bd\dagger}(-\omega,-\omega)C^a(-3\omega) + C^{a\dagger}(+3\omega)F^{bc}(+\omega,+\omega)C^d(+\omega) + C^{d\dagger}(-\omega)F^{bc\dagger}(-\omega,-\omega)C^a(-3\omega)\\
&\qquad - C^{a\dagger}(+3\omega)S^0C^b(+\omega)\varepsilon^{cd}(+\omega,+\omega) - \varepsilon^{cd\dagger}(-\omega,-\omega)C^{b\dagger}(-\omega)S^0C^a(-3\omega) - C^{a\dagger}(+3\omega)S^0C^c(+\omega)\varepsilon^{bd}(+\omega,+\omega)\\
&\qquad - \varepsilon^{bd\dagger}(-\omega,-\omega)C^{c\dagger}(-\omega)S^0C^a(-3\omega) - C^{a\dagger}(+3\omega)S^0C^d(+\omega)\varepsilon^{bc}(+\omega,+\omega) - \varepsilon^{bc\dagger}(-\omega,-\omega)C^{d\dagger}(-\omega)S^0C^a(-3\omega)\\
&\qquad - C^{a\dagger}(+3\omega)S^0C^{cd}(+\omega,+\omega)\varepsilon^b(+\omega) - \varepsilon^{b\dagger}(-\omega)C^{cd\dagger}(-\omega,-\omega)S^0C^a(-3\omega) - C^{a\dagger}(+3\omega)S^0C^{bd}(+\omega,+\omega)\varepsilon^c(+\omega)\\
&\qquad - \varepsilon^{c\dagger}(-\omega)C^{bd\dagger}(-\omega,-\omega)S^0C^a(-3\omega) - C^{a\dagger}(+3\omega)S^0C^{bc}(+\omega,+\omega)\varepsilon^d(+\omega) - \varepsilon^{d\dagger}(-\omega)C^{bc\dagger}(-\omega,-\omega)S^0C^a(-3\omega)\\
&\qquad - C^{b\dagger}(-\omega)S^0C^{cd}(+\omega,+\omega)\varepsilon^a(-3\omega) - \varepsilon^{a\dagger}(+3\omega)C^{cd\dagger}(-\omega,-\omega)S^0C^b(+\omega) - C^{c\dagger}(-\omega)S^0C^{bd}(+\omega,+\omega)\varepsilon^a(-3\omega)\\
&\qquad - \varepsilon^{a\dagger}(+3\omega)C^{bd\dagger}(-\omega,-\omega)S^0C^c(+\omega) - C^{d\dagger}(-\omega)S^0C^{bc}(+\omega,+\omega)\varepsilon^a(-3\omega) - \varepsilon^{a\dagger}(+3\omega)C^{bc\dagger}(-\omega,-\omega)S^0C^d(+\omega)\\
&\qquad + C^{b\dagger}(-\omega)F^a(-3\omega)C^{cd}(+\omega,+\omega) + C^{cd\dagger}(-\omega,-\omega)F^{a\dagger}(+3\omega)C^b(+\omega) + C^{c\dagger}(-\omega)F^a(-3\omega)C^{bd}(+\omega,+\omega)\\
&\qquad + C^{bd\dagger}(-\omega,-\omega)F^{a\dagger}(+3\omega)C^c(+\omega) + C^{d\dagger}(-\omega)F^a(-3\omega)C^{bc}(+\omega,+\omega) + C^{bc\dagger}(-\omega,-\omega)F^{a\dagger}(+3\omega)C^d(+\omega)\}].
\end{aligned} \tag{VIII-1a}$$

$$\begin{aligned}
&\gamma_{abcd}(-3\omega;+\omega,+\omega,+\omega)\\
&\quad= -Tr[n\{U^{a\dagger}(+3\omega)G^b(+\omega)U^{cd}(+\omega,+\omega) + U^{cd\dagger}(-\omega,-\omega)G^{b\dagger}(-\omega)U^a(-3\omega) + U^{a\dagger}(+3\omega)G^c(+\omega)U^{bd}(+\omega,+\omega)\\
&\qquad + U^{bd\dagger}(-\omega,-\omega)G^{c\dagger}(-\omega)U^a(-3\omega) + U^{a\dagger}(+3\omega)G^d(+\omega)U^{bc}(+\omega,+\omega) + U^{bc\dagger}(-\omega,-\omega)G^{d\dagger}(-\omega)U^a(-3\omega)\\
&\qquad - U^{a\dagger}(+3\omega)U^{cd}(+\omega,+\omega)\varepsilon^b(+\omega) - U^{cd\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^{b\dagger}(-\omega) - U^{a\dagger}(+3\omega)U^{bd}(+\omega,+\omega)\varepsilon^c(+\omega)\\
&\qquad - U^{bd\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^{c\dagger}(-\omega) - U^{a\dagger}(+3\omega)U^{bc}(+\omega,+\omega)\varepsilon^d(+\omega) - U^{bc\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^{d\dagger}(-\omega)\}\\
&\qquad + n\{U^{a\dagger}(+3\omega)G^{cd}(+\omega,+\omega)U^b(+\omega) + U^{b\dagger}(-\omega)G^{cd\dagger}(-\omega,-\omega)U^a(-3\omega) + U^{a\dagger}(+3\omega)G^{bd}(+\omega,+\omega)U^c(+\omega)\\
&\qquad + U^{c\dagger}(-\omega)G^{bd\dagger}(-\omega,-\omega)U^a(-3\omega) + U^{a\dagger}(+3\omega)G^{bc}(+\omega,+\omega)U^d(+\omega) + U^{d\dagger}(-\omega)G^{bc\dagger}(-\omega,-\omega)U^a(-3\omega)\\
&\qquad - U^{a\dagger}(+3\omega)U^b(+\omega)\varepsilon^{cd}(+\omega,+\omega) - U^{b\dagger}(-\omega)U^a(-3\omega)\varepsilon^{cd\dagger}(-\omega,-\omega) - U^{a\dagger}(+3\omega)U^c(+\omega)\varepsilon^{bd}(+\omega,+\omega)\\
&\qquad - U^{c\dagger}(-\omega)U^a(-3\omega)\varepsilon^{bd\dagger}(-\omega,-\omega) - U^{a\dagger}(+3\omega)U^d(+\omega)\varepsilon^{bc}(+\omega,+\omega) - U^{d\dagger}(-\omega)U^a(-3\omega)\varepsilon^{bc\dagger}(-\omega,-\omega)\}\\
&\qquad + n\{U^{b\dagger}(-\omega)G^a(-3\omega)U^{cd}(+\omega,+\omega) + U^{cd\dagger}(-\omega,-\omega)G^{a\dagger}(+3\omega)U^b(+\omega) + U^{c\dagger}(-\omega)G^a(-3\omega)U^{bd}(+\omega,+\omega)\\
&\qquad + U^{bd\dagger}(-\omega,-\omega)G^{a\dagger}(+3\omega)U^c(+\omega) + U^{d\dagger}(-\omega)G^a(-3\omega)U^{bc}(+\omega,+\omega) + U^{bc\dagger}(-\omega,-\omega)G^{a\dagger}(+3\omega)U^d(+\omega)\\
&\qquad - U^{b\dagger}(-\omega)U^{cd}(+\omega,+\omega)\varepsilon^a(-3\omega) - U^{cd\dagger}(-\omega,-\omega)U^b(+\omega)\varepsilon^{a\dagger}(+3\omega) - U^{c\dagger}(-\omega)U^{bd}(+\omega,+\omega)\varepsilon^a(-3\omega)\\
&\qquad - U^{bd\dagger}(-\omega,-\omega)U^c(+\omega)\varepsilon^{a\dagger}(+3\omega) - U^{d\dagger}(-\omega)\varepsilon^a(-3\omega)U^{bc}(+\omega,+\omega) - U^{bc\dagger}(-\omega,-\omega)\varepsilon^{a\dagger}(+3\omega)U^d(+\omega)\}].
\end{aligned} \tag{VIII-1b}$$

$$\begin{aligned}
&\gamma_{abcd}(-3\omega;+\omega,+\omega,+\omega)\\
&\quad= Tr[n\{U^a(-3\omega)G^b(+\omega)U^{cd}(+\omega,+\omega) - U^{cd\dagger}(-\omega,-\omega)G^b(+\omega)U^a(-3\omega) + U^a(-3\omega)G^c(+\omega)U^{bd}(+\omega,+\omega)\\
&\qquad - U^{bd\dagger}(-\omega,-\omega)G^c(+\omega)U^a(-3\omega) + U^a(-3\omega)G^d(+\omega)U^{bc}(+\omega,+\omega) - U^{bc\dagger}(-\omega,-\omega)G^d(+\omega)U^a(-3\omega)\\
&\qquad - U^a(-3\omega)U^{cd}(+\omega,+\omega)\varepsilon^b(+\omega) + U^{cd\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^b(+\omega) - U^a(-3\omega)U^{bd}(+\omega,+\omega)\varepsilon^c(+\omega)\\
&\qquad + U^{bd\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^c(+\omega) - U^a(-3\omega)U^{bc}(+\omega,+\omega)\varepsilon^d(+\omega) + U^{bc\dagger}(-\omega,-\omega)U^a(-3\omega)\varepsilon^d(+\omega)\}\\
&\qquad + n\{U^a(-3\omega)G^{cd}(+\omega,+\omega)U^b(+\omega) + U^b(+\omega)G^{cd}(+\omega,+\omega)U^a(-3\omega) + U^a(-3\omega)G^{bd}(+\omega,+\omega)U^c(+\omega)\\
&\qquad + U^c(+\omega)G^{bd}(+\omega,+\omega)U^a(-3\omega) + U^a(-3\omega)G^{bc}(+\omega,+\omega)U^d(+\omega) + U^d(+\omega)G^{bc}(+\omega,+\omega)U^a(-3\omega)\\
&\qquad - U^a(-3\omega)U^b(+\omega)\varepsilon^{cd}(+\omega,+\omega) - U^b(+\omega)U^a(-3\omega)\varepsilon^{cd}(+\omega,+\omega) - U^a(-3\omega)U^c(+\omega)\varepsilon^{bd}(+\omega,+\omega)\\
&\qquad - U^c(+\omega)U^a(-3\omega)\varepsilon^{bd}(+\omega,+\omega) - U^a(-3\omega)U^d(+\omega)\varepsilon^{bc}(+\omega,+\omega) - U^d(+\omega)U^a(-3\omega)\varepsilon^{bc}(+\omega,+\omega)\}\\
&\qquad + n\{U^b(+\omega)G^a(-3\omega)U^{cd}(+\omega,+\omega) - U^{cd\dagger}(-\omega,-\omega)G^a(-3\omega)U^b(+\omega) + U^c(+\omega)G^a(-3\omega)U^{bd}(+\omega,+\omega)\\
&\qquad - U^{bd\dagger}(-\omega,-\omega)G^a(-3\omega)U^c(+\omega) + U^d(+\omega)G^a(-3\omega)U^{bc}(+\omega,+\omega) - U^{bc\dagger}(-\omega,-\omega)G^a(-3\omega)U^d(+\omega)\\
&\qquad - U^b(+\omega)U^{cd}(+\omega,+\omega)\varepsilon^a(-3\omega) + U^{cd\dagger}(-\omega,-\omega)U^b(+\omega)\varepsilon^a(-3\omega) - U^c(+\omega)U^{bd}(+\omega,+\omega)\varepsilon^a(-3\omega)\\
&\qquad + U^{bd\dagger}(-\omega,-\omega)U^c(+\omega)\varepsilon^a(-3\omega) - U^d(+\omega)U^{bc}(+\omega,+\omega)\varepsilon^a(-3\omega) + U^{bc\dagger}(-\omega,-\omega)U^d(+\omega)\varepsilon^a(-3\omega)\}].
\end{aligned} \tag{VIII-1c}$$

DC-EFISHG

$$\begin{aligned}
&\gamma_{abcd}(-2\omega;0,+\omega,+\omega)\\
&\quad= Tr[n\{U^a(-2\omega)G^b(0)U^{cd}(+\omega,+\omega) - U^{cd\dagger}(-\omega,-\omega)G^b(0)U^a(-2\omega) + U^a(-2\omega)G^c(+\omega)U^{bd}(0,+\omega)\\
&\qquad - U^{bd\dagger}(0,-\omega)G^c(+\omega)U^a(-2\omega) + U^a(-2\omega)G^d(+\omega)U^{bc}(0,+\omega) - U^{bc\dagger}(0,-\omega)G^d(+\omega)U^a(-2\omega)\\
&\qquad - U^a(-2\omega)U^{cd}(+\omega,+\omega)\varepsilon^b(0) + U^{cd\dagger}(-\omega,-\omega)U^a(-2\omega)\varepsilon^b(0) - U^a(-2\omega)U^{bd}(0,+\omega)\varepsilon^c(+\omega)\\
&\qquad + U^{bd\dagger}(0,-\omega)U^a(-2\omega)\varepsilon^c(+\omega) - U^a(-2\omega)U^{bc}(0,+\omega)\varepsilon^d(+\omega) + U^{bc\dagger}(0,-\omega)U^a(-2\omega)\varepsilon^d(+\omega)\}\\
&\qquad + n\{U^a(-2\omega)G^{cd}(+\omega,+\omega)U^b(0) + U^b(0)G^{cd}(+\omega,+\omega)U^a(-2\omega) + U^a(-2\omega)G^{bd}(0,+\omega)U^c(+\omega)\\
&\qquad + U^c(+\omega)G^{bd}(0,+\omega)U^a(-2\omega) + U^a(-2\omega)G^{bc}(0,+\omega)U^d(+\omega) + U^d(+\omega)G^{bc}(0,+\omega)U^a(-2\omega)\\
&\qquad - U^a(-2\omega)U^b(0)\varepsilon^{cd}(+\omega,+\omega) - U^b(0)U^a(-2\omega)\varepsilon^{cd}(+\omega,+\omega) - U^a(-2\omega)U^c(+\omega)\varepsilon^{bd}(0,+\omega)\\
&\qquad - U^c(+\omega)U^a(-2\omega)\varepsilon^{bd}(0,+\omega) - U^a(-2\omega)U^d(+\omega)\varepsilon^{bc}(0,+\omega) - U^d(+\omega)U^a(-2\omega)\varepsilon^{bc}(0,+\omega)\}\\
&\qquad + n\{U^b(0)G^a(-2\omega)U^{cd}(+\omega,+\omega) - U^{cd\dagger}(-\omega,-\omega)G^a(-2\omega)U^b(0) + U^c(+\omega)G^a(-2\omega)U^{bd}(0,+\omega)\\
&\qquad - U^{bd\dagger}(0,-\omega)G^a(-2\omega)U^c(+\omega) + U^d(+\omega)G^a(-2\omega)U^{bc}(0,+\omega) - U^{bc\dagger}(0,-\omega)G^a(-2\omega)U^d(+\omega)\\
&\qquad - U^b(0)U^{cd}(+\omega,+\omega)\varepsilon^a(-2\omega) + U^{cd\dagger}(-\omega,-\omega)U^b(0)\varepsilon^a(-2\omega) - U^c(+\omega)U^{bd}(0,+\omega)\varepsilon^a(-2\omega)\\
&\qquad + U^{bd\dagger}(0,-\omega)U^c(+\omega)\varepsilon^a(-2\omega) - U^d(+\omega)U^{bc}(0,+\omega)\varepsilon^a(-2\omega) + U^{bc\dagger}(0,-\omega)U^d(+\omega)\varepsilon^a(-2\omega)\}].
\end{aligned} \tag{VIII-2}$$

IDRI

$$\begin{aligned}
&\gamma_{abcd}(-\omega;+\omega,+\omega,-\omega)\\
&\quad= Tr[n\{U^a(-\omega)G^b(+\omega)U^{cd}(+\omega,-\omega) - U^{cd\dagger}(-\omega,+\omega)G^b(+\omega)U^a(-\omega) + U^a(-\omega)G^c(+\omega)U^{bd}(+\omega,-\omega)\\
&\qquad - U^{bd\dagger}(-\omega,+\omega)G^c(+\omega)U^a(-\omega) + U^a(-\omega)G^d(-\omega)U^{bc}(+\omega,+\omega) - U^{bc\dagger}(-\omega,-\omega)G^d(-\omega)U^a(-\omega)\\
&\qquad - U^a(-\omega)U^{cd}(+\omega,-\omega)\varepsilon^b(+\omega) + U^{cd\dagger}(-\omega,+\omega)U^a(-\omega)\varepsilon^b(+\omega) - U^a(-\omega)U^{bd}(+\omega,-\omega)\varepsilon^c(+\omega)\\
&\qquad + U^{bd\dagger}(-\omega,+\omega)U^a(-\omega)\varepsilon^c(+\omega) - U^a(-\omega)U^{bc}(+\omega,+\omega)\varepsilon^d(-\omega) + U^{bc\dagger}(-\omega,-\omega)U^a(-\omega)\varepsilon^d(-\omega)\}\\
&\qquad + n\{U^a(-\omega)G^{cd}(+\omega,-\omega)U^b(+\omega) + U^b(+\omega)G^{cd}(+\omega,-\omega)U^a(-\omega) + U^a(-\omega)G^{bd}(+\omega,-\omega)U^c(+\omega)\\
&\qquad + U^c(+\omega)G^{bd}(+\omega,-\omega)U^a(-\omega) + U^a(-\omega)G^{bc}(+\omega,+\omega)U^d(-\omega) + U^d(-\omega)G^{bc}(+\omega,+\omega)U^a(-\omega)
\end{aligned}$$

Table VIII. (*Continued*)

$$
\begin{aligned}
&- U^{a}(-\omega)U^{b}(+\omega)\varepsilon^{cd}(+\omega, -\omega) - U^{b}(+\omega)U^{a}(-\omega)\varepsilon^{cd}(+\omega, -\omega) - U^{a}(-\omega)U^{c}(+\omega)\varepsilon^{bd}(+\omega, -\omega)\\
&- U^{c}(+\omega)U^{a}(-\omega)\varepsilon^{bd}(+\omega, -\omega) - U^{a}(-\omega)U^{d}(-\omega)\varepsilon^{bc}(+\omega, +\omega) - U^{d}(-\omega)U^{a}(-\omega)\varepsilon^{bc}(+\omega, +\omega)\}\\
&+ n\{U^{b}(+\omega)G^{a}(-\omega)U^{cd}(+\omega, -\omega) - U^{cd\dagger}(-\omega, +\omega)G^{a}(-\omega)U^{b}(+\omega) + U^{c}(+\omega)G^{a}(-\omega)U^{bd}(+\omega, -\omega)\\
&- U^{bd\dagger}(-\omega, +\omega)G^{a}(-\omega)U^{c}(+\omega) + U^{d}(-\omega)G^{a}(-\omega)U^{bc}(+\omega, +\omega) - U^{bc\dagger}(-\omega, -\omega)G^{a}(-\omega)U^{d}(-\omega)\\
&- U^{b}(+\omega)U^{cd}(+\omega, -\omega)\varepsilon^{a}(-\omega) + U^{cd\dagger}(-\omega, +\omega)U^{b}(+\omega)\varepsilon^{a}(-\omega) - U^{c}(+\omega)U^{bd}(+\omega, -\omega)\varepsilon^{a}(-\omega)\\
&+ U^{bd\dagger}(-\omega, +\omega)U^{c}(+\omega)\varepsilon^{a}(-\omega) - U^{d}(-\omega)U^{bc}(+\omega, +\omega)\varepsilon^{a}(-\omega) + U^{bc\dagger}(-\omega, -\omega)U^{d}(-\omega)\varepsilon^{a}(-\omega)\}]. \qquad \text{(VIII-3)}
\end{aligned}
$$

OKE

$$
\begin{aligned}
&\gamma_{abcd}(-\omega; 0, 0, +\omega)\\
&= Tr[n\{U^{a}(-\omega)G^{b}(0)U^{cd}(0, +\omega) - U^{cd\dagger}(0, -\omega)G^{b}(0)U^{a}(-\omega) + U^{a}(-\omega)G^{c}(0)U^{bd}(0, +\omega)\\
&- U^{bd\dagger}(0, -\omega)G^{b}(0)U^{a}(-\omega) + U^{a}(-\omega)G^{d}(+\omega)U^{bc}(0, 0) - U^{bc\dagger}(0, 0)G^{d}(+\omega)U^{a}(-\omega)\\
&- U^{a}(-\omega)U^{cd}(0, +\omega)\varepsilon^{b}(0) + U^{cd\dagger}(0, -\omega)U^{a}(-\omega)\varepsilon^{b}(0) - U^{a}(-\omega)U^{bd}(0, +\omega)\varepsilon^{c}(0)\\
&+ U^{bd\dagger}(0, -\omega)U^{a}(-\omega)\varepsilon^{c}(0) - U^{a}(-\omega)U^{bc}(0, 0)\varepsilon^{d}(+\omega) + U^{bc\dagger}(0, 0)U^{a}(-\omega)\varepsilon^{d}(+\omega)\}\\
&+ n\{U^{a}(-\omega)G^{cd}(0, +\omega)U^{b}(0) + U^{b}(0)G^{cd}(0, +\omega)U^{a}(-\omega) + U^{a}(-\omega)G^{bd}(0, +\omega)U^{c}(0)\\
&+ U^{c}(0)G^{bd}(0, +\omega)U^{a}(-\omega) + U^{a}(-\omega)G^{bc}(0, 0)U^{d}(+\omega) + U^{d}(+\omega)G^{bc}(0, 0)U^{a}(-\omega)\\
&- U^{a}(-\omega)U^{b}(0)\varepsilon^{cd}(0, +\omega) - U^{b}(0)U^{a}(-\omega)\varepsilon^{cd}(0, +\omega) - U^{a}(-\omega)U^{c}(0)\varepsilon^{bd}(0, +\omega)\\
&- U^{c}(0)U^{a}(-\omega)\varepsilon^{bd}(0, +\omega) - U^{a}(-\omega)U^{d}(+\omega)\varepsilon^{bc}(0, 0) - U^{d}(+\omega)U^{a}(-\omega)\varepsilon^{bc}(0, 0)\}\\
&+ n\{U^{b}(0)G^{a}(-\omega)U^{cd}(0, +\omega) - U^{cd\dagger}(0, -\omega)G^{a}(-\omega)U^{b}(0) + U^{c}(0)G^{a}(-\omega)U^{bd}(0, +\omega)\\
&- U^{bd\dagger}(0, -\omega)G^{a}(-\omega)U^{c}(0) + U^{d}(+\omega)G^{a}(-\omega)U^{bc}(0, 0) - U^{bc\dagger}(0, 0)G^{a}(-\omega)U^{d}(+\omega)\\
&- U^{b}(0)U^{cd}(0, +\omega)\varepsilon^{a}(-\omega) + U^{cd\dagger}(0, -\omega)U^{b}(0)\varepsilon^{a}(-2\omega) - U^{c}(0)U^{bd}(0, +\omega)\varepsilon^{a}(-\omega)\\
&+ U^{bd\dagger}(0, -\omega)U^{c}(0)\varepsilon^{a}(-\omega) - U^{d}(+\omega)U^{bc}(0, 0)\varepsilon^{a}(-\omega) + U^{bc\dagger}(0, 0)U^{d}(+\omega)\varepsilon^{a}(-\omega)\}]. \qquad \text{(VIII-4)}
\end{aligned}
$$

DC-EFIOR

$$
\begin{aligned}
&\gamma_{abcd}(0; 0, +\omega, -\omega)\\
&= Tr[n\{U^{a}(0)G^{b}(0)U^{cd}(+\omega, -\omega) - U^{cd\dagger}(-\omega, +\omega)G^{b}(0)U^{a}(0) + U^{a}(0)G^{c}(+\omega)U^{bd}(0, -\omega)\\
&- U^{bd\dagger}(0, +\omega)G^{c}(+\omega)U^{a}(0) + U^{a}(0)G^{d}(-\omega)U^{bc}(0, +\omega) - U^{bc\dagger}(0, -\omega)G^{d}(-\omega)U^{a}(0)\\
&- U^{a}(0)U^{cd}(+\omega, -\omega)\varepsilon^{b}(0) + U^{cd\dagger}(-\omega, +\omega)U^{a}(0)\varepsilon^{b}(0) - U^{a}(0)U^{bd}(0, -\omega)\varepsilon^{c}(+\omega)\\
&+ U^{bd\dagger}(0, +\omega)U^{a}(0)\varepsilon^{c}(+\omega) - U^{a}(0)U^{bc}(0, +\omega)\varepsilon^{d}(-\omega) + U^{bc\dagger}(0, -\omega)U^{a}(0)\varepsilon^{d}(-\omega)\}\\
&+ n\{U^{a}(0)G^{cd}(+\omega, -\omega)U^{b}(0) + U^{b}(0)G^{cd}(+\omega, -\omega)U^{a}(0) + U^{a}(0)G^{bd}(0, -\omega)U^{c}(+\omega)\\
&+ U^{c}(+\omega)G^{bd}(0, -\omega)U^{a}(0) + U^{a}(0)G^{bc}(0, +\omega)U^{d}(-\omega) + U^{d}(-\omega)G^{bc}(0, +\omega)U^{a}(0)\\
&- U^{a}(0)U^{b}(0)\varepsilon^{cd}(+\omega, -\omega) - U^{b}(0)U^{a}(0)\varepsilon^{cd}(+\omega, -\omega) - U^{a}(0)U^{c}(+\omega)\varepsilon^{bd}(0, -\omega)\\
&- U^{c}(+\omega)U^{a}(0)\varepsilon^{bd}(0, -\omega) - U^{a}(0)U^{d}(-\omega)\varepsilon^{bc}(0, +\omega) - U^{d}(-\omega)U^{a}(0)\varepsilon^{bc}(0, +\omega)\}\\
&+ n\{U^{b}(0)G^{a}(0)U^{cd}(+\omega, -\omega) - U^{cd\dagger}(-\omega, +\omega)G^{a}(0)U^{b}(0) + U^{c}(+\omega)G^{a}(0)U^{bd}(0, -\omega)\\
&- U^{bd\dagger}(0, +\omega)G^{a}(0)U^{c}(+\omega) + U^{d}(-\omega)G^{a}(0)U^{bc}(0, +\omega) - U^{bc\dagger}(0, -\omega)G^{a}(0)U^{d}(-\omega)\\
&- U^{b}(0)U^{cd}(+\omega, -\omega)\varepsilon^{a}(0) + U^{cd\dagger}(-\omega, +\omega)U^{b}(0)\varepsilon^{a}(0) - U^{c}(+\omega)U^{bd}(0, -\omega)\varepsilon^{a}(0)\\
&+ U^{bd\dagger}(0, +\omega)U^{c}(+\omega)\varepsilon^{a}(0) - U^{d}(-\omega)U^{bc}(0, +\omega)\varepsilon^{a}(0) + U^{bc\dagger}(0, -\omega)U^{d}(-\omega)\varepsilon^{a}(0)\}]. \qquad \text{(VIII-5)}
\end{aligned}
$$

Static second hyperpolarizability

$$
\begin{aligned}
&\gamma_{abcd}(0; 0, 0, 0)\\
&= Tr[n\{U^{a}(0)G^{b}(0)U^{cd}(0, 0) - U^{cd\dagger}(0, 0)G^{b}(0)U^{a}(0) + U^{a}(0)G^{c}(0)U^{bd}(0, 0) - U^{bd\dagger}(0, 0)G^{c}(0)U^{a}(0)\\
&+ U^{a}(0)G^{d}(0)U^{bc}(0, 0) - U^{bc\dagger}(0, 0)G^{d}(0)U^{a}(0) - U^{a}(0)U^{cd}(0, 0)\varepsilon^{b}(0) + U^{cd\dagger}(0, 0)U^{a}(0)\varepsilon^{b}(0)\\
&- U^{a}(0)U^{bd}(0, 0)\varepsilon^{c}(0) + U^{bd\dagger}(0, 0)U^{a}(0)\varepsilon^{c}(0) - U^{a}(0)U^{bc}(0, 0)\varepsilon^{d}(0) + U^{bc\dagger}(0, 0)U^{a}(0)\varepsilon^{d}(0)\}\\
&+ n\{U^{a}(0)G^{cd}(0, 0)U^{b}(0) + U^{b}(0)G^{cd}(0, 0)U^{a}(0) + U^{a}(0)G^{bd}(0, 0)U^{c}(0) + U^{c}(0)G^{bd}(0, 0)U^{a}(0)\\
&+ U^{a}(0)G^{bc}(0, 0)U^{d}(0) + U^{d}(0)G^{bc}(0, 0)U^{a}(0) + U^{a}(0)U^{b}(0)\varepsilon^{cd}(0, 0) - U^{b}(0)U^{a}(0)\varepsilon^{cd}(0, 0)\\
&- U^{a}(0)U^{c}(0)\varepsilon^{bd}(0, 0) - U^{c}(0)U^{a}(0)\varepsilon^{bd}(0, 0) - U^{a}(0)U^{d}(0)\varepsilon^{bc}(0, 0) - U^{d}(0)U^{a}(0)\varepsilon^{bc}(0, 0)\}\\
&+ n\{U^{b}(0)G^{a}(0)U^{cd}(0, 0) - U^{cd\dagger}(0, 0)G^{a}(0)U^{b}(0) + U^{c}(0)G^{a}(0)U^{bd}(0, 0) - U^{bd\dagger}(0, 0)G^{a}(0)U^{c}(0)\\
&+ U^{d}(0)G^{a}(0)U^{bc}(0, 0) - U^{bc\dagger}(0, 0)G^{a}(0)U^{d}(0) - U^{b}(0)U^{cd}(0, 0)\varepsilon^{a}(0) + U^{cd\dagger}(0, 0)U^{b}(0)\varepsilon^{a}(0)\\
&- U^{c}(0)U^{bd}(0, 0)\varepsilon^{a}(0) + U^{bd\dagger}(0, 0)U^{c}(0)\varepsilon^{a}(0) - U^{d}(0)U^{bc}(0, 0)\varepsilon^{a}(0) + U^{bc\dagger}(0, 0)U^{d}(0)\varepsilon^{a}(0)\}]. \qquad \text{(VIII-6)}
\end{aligned}
$$

is achieved. The *abcd* component of γ is calculated for example, for THG from eq. (IV-3d).

Noniterative Calculations

The noniterative calculations of the various βs and γs as given in eqs. (VII-1, 2, 3, 4) and eqs. (VIII-1c, 2, 3, 4, 5, 6), respectively are rather simple and need only few extra calculations at the first order level. Thus, for the calculations of $\beta_{abc}(-2\omega; +\omega, +\omega)$ the first-order equation is solved with frequencies $+\omega$ and $+2\omega$ and the resulting $U(+2\omega)$, and $G(+2\omega)$ matrices are stored to be used with eq. (55). For the calculation of $\gamma_{abcd}(-3\omega; +\omega, +\omega, +\omega)$ again the first order equation is solved with frequency $+3\omega$ and the corresponding $U(+3\omega)$ and $G(+3\omega)$ matrices are stored to be used in eq. (VIII-1c). The same first order parameters with frequency $+2\omega$ as calculated for the SHG are used for the calculation of $\gamma_{abcd}(-2\omega; 0, +\omega, +\omega)$ together with the second order parameters. For the calculation of γs second order equations are solved iteratively as described in the previous section and the resulting U, G, and ε matrices are stored. Using the first and the second order parameters then the γs are calculated from eq. (VIII-1c) through eq. (VIII-6).

With the options available in the program one can choose to compute or ignore any of the first-, second-, or the third-order effects with the condition that if a particular higher-order effect is to be solved, the lower-order matrices needed for the computation of the constant part of the density and U matrices in the iterative calculation and β or γ in the noniterative calculation must be available from the corresponding solution.

CONCLUSION

Time-dependent CPHF theory has been applied to obtain analytical expressions for nonlinear optical processes up to third order. The corresponding code, which is implemented in the HONDO program package has been described. The program has also been successfully used for the haloform series and nitroaniline with more than 200 functions in the basis set and is general enough to be applied to larger systems containing several hundred basis functions. The results of the applications to haloform and nitroaniline will be reported elsewhere.[50]

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APPENDIX A

The energy $E(\mathbf{E})$ of a molecular system perturbed by an external electric field $\mathbf{E}$ can be written as:

$$E(\mathbf{E}) = E^0 - \mu_a E^a - (2!)^{-1}\alpha_{ab}E^aE^b - (3!)^{-1} \times \beta_{abc}E^aE^bE^c - (4!)^{-1}\gamma_{abcd}E^aE^bE^cE^d - \cdots, \quad \text{(A-1)}$$

where the summation over repeated indices is implied. The indices $a, b, c, d, \ldots = x, y, z$. In the above equation, μ_a is the a component of the dipole moment, α_{ab}, β_{abc}, and γ_{abcd} are respectively, the components of polarizability, hyperpolarizability and second hyperpolarizability tensors. A component of the total dipole moment p^a is obtained from the first derivative $(\partial E(\mathbf{E})/\partial E^a)$, so that from eq. (A-1)

$$p^a = -\mu_a - \alpha_{ab}E^b - (2!)^{-1}\beta_{abc}E^bE^c - (3!)^{-1}\gamma_{abcd}E^bE^cE^d - \cdots \quad \text{(A-2)}$$

The quantum mechanical expression for the component of the total dipole moment, p^a is written as

$$p^a = \langle \Psi | \mathcal{H}^a | \Psi \rangle, \quad \text{(A-3)}$$

where

$$\mathcal{H}^a = \frac{\partial \mathcal{H}}{\partial E^a}, \quad \text{(A-4)}$$

and

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'. \quad \text{(A-5)}$$

$\mathcal{H}^0$ and $\mathcal{H}'$ in eq (A-5) are defined in eq. (4) and eq. (2), respectively. Using eqs. (2), (2a) and (4) with eqs. (A-4) and (A-5), one gets

$$\mathcal{H}^a = -\sum_i^N (e \cdot a_j). \quad \text{(A-6)}$$

Substituting eq. (A-6) into eq. (A-3) and writing the molecular wave function Ψ in terms of the MO coefficient and basis function matrices and using eq. (10), eq. (A-3) can be written as

$$p^a = Tr[H^aD], \quad \text{(A-7)}$$

where Tr stands for the trace defined as

$$TrA = \sum_i^{\text{all}} A_{ii}, \quad \text{(A-8)}$$

and H^a is the dipole moment matrix, defined over the basis functions χs as

$$H^a_{st}(1) = -(\chi_s(1)|e \cdot a_1|\chi_t(1)). \quad \text{(A-9)}$$

After substituting eq. (17d) into eq. (A-7), we get

$$p^a = Tr[H^aD^0] + Tr[H^aD^b]E^b + (2!)^{-1}Tr[H^aD^{bc}]E^bE^c + (3!)^{-1}Tr[H^aD^{bcd}]E^bE^cE^d + \cdots \quad \text{(A-10)}$$

Comparing eq. (A-2) and eq. (A-10) we get

$$\mu_a = -Tr[H^aD^0]. \quad \text{(A-11)}$$

$$\alpha_{ab} = -Tr[H^aD^b]. \quad \text{(A-12)}$$

$$\beta_{abc} = -Tr[H^aD^{bc}]. \quad \text{(A-13)}$$

$$\gamma_{abcd} = -Tr[H^aD^{bcd}]. \quad \text{(A-14)}$$

Thus the polarizability and hyperpolarizabilities can be obtained from the dipole moment matrix and the perturbed density matrices. For static case ($\omega = 0$) eqs. (A-12) to (A-14) directly give the static polarizability and the hyperpolarizabilities. For dynamic cases ($\omega \neq 0$), substitution of the frequency dependent perturbed density matrices in eqs. (A-12) to (A-14) gives the polarizability and hyperpolarizabilities for the corresponding nonlinear phenomena.

APPENDIX B

We denote the expectation value of an operator A by

$$\langle A \rangle = 2 \sum_i^{\text{occ}} A_{ii}, \quad \text{(B-1)}$$

where occ represents the set of occupied orbitals, and A_{ii} is the matrix value of A for the orbital i. If n represents the occupation number matrix, i.e., a diagonal matrix with the first occ elements set to 2 and the other diagonal elements set to zero, we find that

$$\langle A \rangle = Tr[nA], \quad \text{(B-2)}$$

where Tr is the usual trace operator defined as

$$Tr[A] = \sum_{i}^{\text{all}} A_{ii}, \qquad \text{(B-3)}$$

which satisfies the well known property

$$Tr[AB] = Tr[BA]. \qquad \text{(B-4)}$$

APPENDIX C

In eq. (55) we have to evaluate two types of terms. A generic form of the first terms yields

$$Tr[nU^aG^bU^c] = 2\sum_{i}^{\text{occ}}\sum_{kl}^{\text{all}} U^a_{ik}G^b_{kl}U^c_{li}. \qquad \text{(C-1)}$$

A generic form of the second terms yields

$$Tr[nU^aU^c\varepsilon^b] = 2\sum_{i}^{\text{occ}}\sum_{kl}^{\text{all}} U^a_{ik}U^c_{kl}\varepsilon^b_{li}. \qquad \text{(C-2)}$$

Because of the block diagonal form of ε^b, the l summation in eq. (C-2) can be reduced to the range of the occupied orbitals, i.e.,

$$Tr[nU^aU^c\varepsilon^b] = 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{all}}\sum_{l}^{\text{occ}} U^a_{ik}U^c_{kl}\varepsilon^b_{li}. \qquad \text{(C-3)}$$

Eq. (C-3) can be written as

$$Tr[nU^aU^c\varepsilon^b] = 2\sum_{k}^{\text{all}}\sum_{il}^{\text{occ}} U^c_{kl}\varepsilon^b_{li}U^a_{ik}. \qquad \text{(C-4)}$$

In this form the summations of eq. (C-1) and eq. (C-4) can be accomplished through the same subroutine with the summation index only being different.

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