

Chapter 2

Quantum-Mechanical Treatment of Responses to Electric Fields—Molecular Systems

Abstract In this chapter we first give a brief overview of theoretical methods for calculating the responses of smaller or larger, finite systems to electric fields. Subsequently, we concentrate on the quantum-mechanical (coupled) perturbation theory treatment of these systems. Both electronic and vibrational responses are discussed.

2.1 Introduction

In parallel with the many experimental studies of linear and non-linear optical properties, some of which were mentioned in the previous chapter, there has also been much theoretical work. We do not intend to describe all that has been done (for a relatively recent review, see [1]) but will present in this chapter an overview of the quantum-mechanical methods used to treat the electronic and nuclear responses to applied electric fields. These responses determine the linear and nonlinear optical (L&NLO) properties. Although the methodology has been developed in connection with ordinary small and medium-size molecules, our emphasis will be on treatments that are most readily extended to large systems, since the latter are of primary interest in this monograph.

The response of any system to applied electric fields, static and/or dynamic, can be calculated by solving the time-dependent Schrödinger equation

$$\left[\hat{H}_0(\mathbf{X}, \mathbf{x}) + \hat{H}'(\mathbf{X}, \mathbf{x}, t) \right] \Psi(\mathbf{X}, \mathbf{x}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{X}, \mathbf{x}, t). \quad (2.1)$$

Here $\hat{H}_0$ is the Hamilton operator for the field-free system, whereas the effect of the field(s) is described through $\hat{H}'$ (Sect. 2.3 and Chap. 3). The L&NLO properties of concern here are defined in terms of a power series expansion for the response to the latter. In Eq. (2.1) $\mathbf{X}$ denotes the set of nuclear coordinates, whereas $\mathbf{x}$ serves the same role for the electronic coordinates. We have assumed that $\hat{H}_0$ does not contain any explicit time dependence and, for sake of simplicity, relativistic effects are ignored (i.e. there are no terms in the Hamiltonian involving electron spin operators).

Within the Born-Oppenheimer approximation, the solutions of the field-free time-independent Schrödinger equation may be written as products of electronic and

vibrational, i.e. vibronic, wavefunctions where the electronic wavefunction satisfies

$$\hat{H}_e^0(\mathbf{X}; \mathbf{x}) \Phi_K^0(\mathbf{X}; \mathbf{x}) = E_K^0(\mathbf{X}) \Phi_K^0(\mathbf{X}; \mathbf{x}). \quad (2.2)$$

In the above equation the electronic Hamiltonian, $\hat{H}_e^0(\mathbf{X}; \mathbf{x})$, is the same as $\hat{H}_0$ except that the nuclear kinetic energy term has been removed. Besides the electronic kinetic energy this Hamiltonian contains the electrostatic potential for interaction between the electrons and nuclei as well as the electron-electron and nuclear-nuclear repulsion, all evaluated at a fixed geometry. Thus, $E_K^0(\mathbf{X})$ and $\Phi_K^0(\mathbf{X}; \mathbf{x})$ depend parametrically on the positions of the nuclei. Using the electronic wavefunctions of Eq. (2.2) as the basis for a time-dependent perturbation treatment of $\hat{H}'(\mathbf{X}, \mathbf{x}, t)$ one can obtain the conventional clamped nucleus (CN) sum-over-state (SOS) expressions presented in Sect. 2.3 for the time- or frequency-dependent electronic (hyper)polarizabilities at, say, the ground state equilibrium geometry. These expressions are approximate, even when zero point vibrational averaging is included, because the effect of non-adiabatic coupling with simultaneous vibrational motions is ignored [2]. Nonetheless, in the cases that have been studied the CN approximation has proved to be quite accurate and, almost without exception, is used in the SOS treatment of electronic L&NLO properties as it is here.

SOS calculations require determining the entire set of excited electronic states, which is impractical for ab initio treatment of large (or, even, medium-size) systems. Such calculations have been widely employed, however, at the semi-empirical level [3], and/or in cases where it is assumed that only a few key states are important (e.g. 2-state approximation for β), or when approximate ab initio excited states are taken to be sufficient (e.g. in the uncoupled Hartree-Fock method discussed briefly in Sect. 2.5). As a result, SOS expressions can be useful for qualitative analysis. They have also proved valuable for other purposes as mentioned in Sect. 2.2.

At the ab initio level, for large systems it is preferable to employ either the time-dependent Hartree-Fock (TDHF) or time-dependent Kohn-Sham DFT (TDDFT) procedure. In Sect. 2.3 the general formulation of these two analytical single-particle methods is outlined. Then, in Sect. 2.4, we present the resulting perturbation theory equations in compact form and describe the strategy for solving them. In passing we note that, beyond TDHF, any correlated wavefunction method (MP2, MCSCF, CCSD, ...) can be adapted for calculating electronic L&NLO properties, although these procedures are much more readily applicable to smaller systems.

The electronic response to a static external field is a special case. In that event the clamped nucleus electronic (hyper)polarizabilities can alternatively be obtained numerically by means of the finite field (FF) method. In the FF method the perturbation term [$\hat{H}'(\mathbf{X}, \mathbf{x}, 0)$ in Eq. (2.1)] is included directly in $\hat{H}_e$. Calculations are carried out for different field magnitudes, as well as directions, and then, the electronic response is fit to a power series in the magnitude for each desired direction. In principle, the FF approach can be extended to the time domain to find dynamic electronic (hyper)polarizabilities as well.

As implied above, there is a separate nuclear (i.e. vibrational) response that contributes to the (hyper)polarizabilities. It is the subject of Sect. 2.5. This contribu-

tion appears in the theory when one takes into account the vibrational component of the Born-Oppenheimer vibronic wavefunction. Then, it is readily seen that the sum-over- (vibronic) states contains terms due to vibrational excitations on the ground electronic state potential energy surface [4]. In contrast with the small error in the electronic (hyper)polarizabilities due to the CN approximation, the effect of these vibrational response terms can be important—sometimes much more so than the CN electronic terms—as will be seen in Sect. 2.5, where the role of FF calculations in determining this effect will be elucidated.

2.2 Clamped Nucleus Sum-Over-States Electronic (Hyper)polarizabilities

In order to obtain an expression for the electronic (hyper)polarizabilities we clamp the nuclear coordinates at $\mathbf{X} = \mathbf{X}_0$. Then, in the field-free case, the time-dependent solutions of the electronic Schrödinger equation may be written as

$$\Phi_K^0(\mathbf{X}_0; \mathbf{x}, t) = \exp(-iE_K^0 t/\hbar) \Phi_K^0(\mathbf{X}_0; \mathbf{x}) \quad (2.3)$$

where $\Phi_K^0(\mathbf{X}_0, \mathbf{x})$ and $E_K^0 = E_K^0(\mathbf{X}_0)$ are the stationary state solutions of Eq. (2.2). For spatially uniform oscillating electric fields ($\omega = 0$ in static limit),

$$\mathbf{E}(t) = \sum_{\omega} [\mathbf{E}_{+\omega} e^{+i\omega t} + \mathbf{E}_{-\omega} e^{-i\omega t}], \text{ with } \mathbf{E}_{+\omega} = \mathbf{E}_{-\omega}, \quad (2.4)$$

the scalar interaction with the molecular dipole moment operator ($-e$ is the electronic charge and eZ_A the charge of nucleus A)

$$\hat{\mu}(\mathbf{X}_0, \mathbf{x}) = -e \sum_i \mathbf{x}_i + e \sum_A Z_A \mathbf{X}_{A,0} \quad (2.5)$$

is given by:

$$\hat{H}'(\mathbf{X}_0, \mathbf{x}, t) = -\hat{\mu}(\mathbf{X}_0, \mathbf{x}) \cdot \mathbf{E}(t). \quad (2.6)$$

As shown by Orr and Ward [5], a standard time-dependent perturbation theory treatment of Eqs. (2.1), (2.3) and (2.6), assuming resonance-induced excited state populations and damping are negligible, leads to the following sum-over-states (SOS) formulas for the dynamic (i.e. frequency-dependent) (hyper)polarizabilities

$$\alpha_{\zeta\eta}(-\omega_{\sigma}; \omega) = \frac{1}{\hbar} \sum_{\sigma} P_{-\sigma,1} \sum_K' \frac{1}{\omega_K - \omega_{\sigma}} \langle 0 | \hat{\mu}_{\zeta} | K \rangle \langle K | \hat{\mu}_{\eta} | 0 \rangle \quad (2.7)$$

$$\beta_{\zeta\eta\kappa}(-\omega_\sigma; \omega_1, \omega_2) = \frac{1}{\hbar^2} \sum P_{-\sigma,1,2} \sum_K' \sum_L' \frac{1}{(\omega_K - \omega_\sigma)(\omega_L - \omega_2)} \times \langle 0 | \hat{\mu}_\zeta | K \rangle \langle K | \tilde{\mu}_\eta | L \rangle \langle L | \hat{\mu}_\kappa | 0 \rangle \quad (2.8)$$

$$\begin{aligned} \gamma_{\zeta\eta\kappa\lambda}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = & \frac{1}{\hbar^3} \sum P_{-\sigma,1,2,3} \\ & \left[\sum_K' \sum_L' \sum_M' \frac{1}{(\omega_K - \omega_\sigma)(\omega_L - \omega_2 - \omega_3)(\omega_M - \omega_3)} \right. \\ & \times \langle 0 | \hat{\mu}_\zeta | K \rangle \langle K | \tilde{\mu}_\eta | L \rangle \langle L | \tilde{\mu}_\kappa | M \rangle \langle M | \hat{\mu}_\delta | 0 \rangle \\ & - \sum_K' \sum_L' \frac{1}{(\omega_K - \omega_\sigma)(\omega_L - \omega_3)(\omega_L + \omega_2)} \\ & \left. \times \langle 0 | \hat{\mu}_\zeta | K \rangle \langle K | \hat{\mu}_\eta | 0 \rangle \langle 0 | \hat{\mu}_\kappa | L \rangle \langle L | \hat{\mu}_\lambda | 0 \rangle \right]. \quad (2.9) \end{aligned}$$

In Eqs. (2.7), (2.8) and (2.9) α is the linear polarizability, β is the first hyperpolarizability, and γ is the second hyperpolarizability. The symbol $\beta_{\zeta\eta\kappa}(-\omega_\sigma; \omega_1, \omega_2)$, for example, indicates the $\zeta\eta\kappa$ tensor component of the first hyperpolarizability for applied fields of frequency ω_1 (in the Cartesian direction η) and ω_2 (in the direction κ); $\omega_\sigma = \omega_1 + \omega_2$ is the frequency of the induced dipole moment (in the direction ζ); and $\sum P_{-\sigma,1,2}$ represents a sum over the 6 permutations of the pairs $(-\omega_\sigma/\hat{\mu}_\zeta, \omega_1/\hat{\mu}_\eta, \text{ and } \omega_2/\hat{\mu}_\kappa)$. We use primes on the sums over K, L to indicate that the ground electronic state $|0\rangle$ is excluded. The quantity $\hbar\omega_K$ is the energy of electronic state $|K\rangle$ relative to $|0\rangle$, and $\hat{\mu} = \hat{\mu} - \langle 0 | \hat{\mu} | 0 \rangle$. An exactly analogous interpretation applies to Eqs. (2.7) and (2.9).

In general, the SOS expressions are too inefficient computationally for quantitative purposes, but they can be useful for qualitative analysis as mentioned in the overview preceding this section. Moreover, they often serve as the basis for the formulation of: (i) resonant NLO processes such as two-photon absorption [$\omega_2 = \omega_3 = \omega = \omega_\sigma$ and $\omega_L = 2\omega$ in the first term of Eq. (2.9)]; (ii) vibrational (hyper)polarizabilities (see Sect. 2.5); and (iii) physical limits on off-resonance electronic (hyper)polarizabilities [6, 7]. Finally, if $|0\rangle$ is the Hartree-Fock (HF) wavefunction, then the SOS formulas become equivalent to an uncoupled time-dependent Hartree-Fock (UC-TDHF) perturbation treatment.

2.3 Time-Dependent Hartree-Fock and DFT (Clamped Nucleus) Electronic Properties

The UC-TDHF perturbation method mentioned in the previous section does not account for orbital relaxation, i.e. the change in the HF density matrix (see below) induced by the applied fields. Such orbital relaxation is included in the (coupled) TDHF treatment and, typically, makes an important contribution to the calculated

electronic linear and nonlinear (L&NLO) optical properties. In the limit of static fields the TDHF method is often referred to as coupled perturbed Hartree Fock (CPHF).

There are a number of alternative analytical procedures for carrying out a TDHF, also known as the Random Phase Approximation (RPA), treatment (see, e.g. [8–10]). In fact, TDHF=RPA is the simplest version of the (more general) ‘response method’, often developed using polarization propagators [11, 12]. For the treatment of large systems this simplest (i.e. TDHF) version is the most useful. One convenient formulation of TDHF in the non-resonant regime is the following procedure due to Karna and Dupuis [9] (see references cited therein for earlier work). Using a single determinant wavefunction for $|K\rangle = |0\rangle$ in Eq. (2.2), and variationally optimizing the HF orbitals ($\psi_i^{(0)}$), leads to the usual field-free Fock equation (in matrix form)

$$\underline{\underline{F}}^{(0)} \underline{\underline{C}}^{(0)} = \underline{\underline{S}}^{(0)} \underline{\underline{C}}^{(0)} \underline{\underline{\epsilon}}^{(0)}, \quad \left(\underline{\underline{C}}^{(0)\dagger} \underline{\underline{S}}^{(0)} \underline{\underline{C}}^{(0)} = \underline{\underline{1}} \right) \quad (2.10)$$

where $\underline{\underline{C}}^{(0)}$ is the matrix of expansion coefficients that transform the basis functions $\underline{\underline{\chi}}$ into molecular orbitals $\underline{\underline{\psi}}^{(0)}$,

$$\psi_i^{(0)}(\mathbf{X}_0, \mathbf{x}) = \sum_j \chi_j(\mathbf{X}_0, \mathbf{x}) C_{ji}^{(0)}(\mathbf{X}_0) \quad (2.11)$$

or

$$\underline{\underline{\psi}}^{(0)} = \underline{\underline{\chi}} \underline{\underline{C}}^{(0)}. \quad (2.12)$$

In Eq. (2.10) $\underline{\underline{\epsilon}}^{(0)}$ is normally (=the canonical choice) taken to be a diagonal matrix of Lagrange multipliers—also known as orbital energies). Moreover, $\underline{\underline{S}}^{(0)}$ is the overlap matrix,

$$S_{ij}^{(0)} = \langle \chi_i | \chi_j \rangle \quad (2.13)$$

and, assuming that all occupied molecular orbitals are doubly occupied,

$$\begin{aligned} F_{ij}^{(0)} &= \langle \chi_i(1) | \hat{h}(1) | \chi_j(1) \rangle \\ &+ \sum_{kl} \left[\langle \chi_i(1) \chi_k(2) | \frac{1}{r_{12}} | \chi_j(1) \chi_l(2) \rangle - \frac{1}{2} \langle \chi_i(1) \chi_k(2) | \frac{1}{r_{12}} | \chi_l(1) \chi_j(2) \rangle \right] D_{kl}^{(0)}. \end{aligned} \quad (2.14)$$

The operator $\hat{h}(1)$ here contains the one-electron kinetic energy and nuclear-electron attraction terms while the remaining terms on the rhs, due to electron-electron repulsion, consist of two-electron integrals each multiplied by an element of the density matrix

$$\underline{\underline{D}}^{(0)} = \underline{\underline{C}}^{(0)} \underline{\underline{n}} \underline{\underline{C}}^{(0)\dagger} \quad (2.15)$$

where $\underline{\underline{n}}$ is the diagonal occupation matrix containing the eigenvalues 2 for occupied orbitals and 0 for unoccupied orbitals. It is straightforward to extend the above equations to unrestricted Hartree-Fock with singly-occupied spin-orbitals.

When the perturbation due to the terms in Eq. (2.6) is taken into account the time-dependent Schrödinger equation must be utilized. Thus, $i \underline{\underline{S}}^{(0)} \frac{\partial}{\partial t} \underline{\underline{C}}$ must be added to the rhs of Eq. (2.10) and the perturbed coefficient matrix (which depends upon the frequency and direction of the field), as well as the corresponding matrix of Lagrange multipliers, becomes time-dependent. At the same time, it is convenient to retain the normalization condition so that ($S = S^{(0)}$):

$$\underline{\underline{C}}^\dagger \underline{\underline{S}} \underline{\underline{C}} = \underline{\underline{C}}^{(0)\dagger} \underline{\underline{S}} \underline{\underline{C}}^{(0)} = \underline{\underline{1}}. \quad (2.16)$$

Subsequently, we may expand all field-dependent quantities in the Fock equation (2.10) (the basis functions $\underline{\underline{\chi}}$ are assumed here, and above, to be field-independent) as power series in $E_\omega e^{\pm i\omega t}$. Then, terms on either side of this equation, that are of like power in the field and have the same exponential frequency factor, are equated to one another. This leads to the TDHF perturbation equations, which will be presented in a compact form in the next section. The general strategy for solving them is described below with more details given later.

For non-resonant frequencies well below the first electronic absorption the first-order TDHF perturbation equation for the coefficient matrix may be solved self-consistently starting with the uncoupled approximation. This matrix (as well as the matrix of Lagrange multipliers) is determined only up to an arbitrary unitary transformation amongst the occupied (and/or amongst unoccupied) molecular orbitals. In order to ensure stable solutions a non-canonical choice is made whereby $\underline{\underline{\varepsilon}}$ has non-zero off-diagonal elements in first-order connecting different occupied (as well as different unoccupied) molecular orbitals, while maintaining the fact that there are no elements connecting the block of occupied orbitals with the block of unoccupied orbitals. The non-zero off-diagonal elements of the Lagrange multiplier matrix within the occupied and unoccupied blocks are determined by the orthonormality condition for the first-order coefficients, which is enforced in a particularly simple manner (see Sect. 2.4). The second-order perturbation equations may be solved similarly using the first-order solutions and a computationally convenient non-canonical choice for the second-order Lagrange multipliers (similar to what is done in first-order). Explicit expressions for the non-canonical perturbation treatment are provided in the next section.

Finally, the total (permanent + field-induced) dipole moment is just the average value of the dipole moment operator

$$\mu = \sum_{ij} \langle \chi_i | \hat{\mu} | \chi_j \rangle D_{ji} = \text{Tr}(\underline{\underline{\mathbf{M}}} \underline{\underline{D}}). \quad (2.17)$$

Here $\underline{\underline{D}}$ is the total density matrix. Hence, the terms in $\underline{\underline{D}}$ that are linear in the field determine the linear polarizability tensor; the quadratic terms determine the first hyperpolarizability tensor; etc. These are the $n + 1$ expressions for the (hyper)polarizabilities. As in the time-independent case, the TDHF perturbation theory equations can be manipulated to yield a $2n + 1$ rule whereby not only the linear polarizability, but also the first hyperpolarizability (a third-order property) can be obtained from solutions of the first-order perturbation equations. For the second (hyper)polarizability, however, the second-order (but not third-order) solutions must be known as well. The $2n + 1$ formulas for the NLO hyperpolarizabilities induced by a monochromatic applied field, with and without an additional static (i.e., DC) field may be found in Tables VII and VIII of [9]. These formulas may readily be extended to cover the general case when there is more than one laser source each operating at its own frequency.

The TDHF method is a wavefunction approach that, by definition, does not take account of electron correlation. Correlation can be introduced through any of the standard quantum-chemical methods that have been extended to take into account time-dependence. This includes Møller-Plesset (MP) perturbation theory and coupled cluster methods, as well as the multi-configuration self-consistent field and configuration interaction treatments. There are also higher-order linear response/polarization propagator methods. As noted above, TDHF corresponds to the simplest possible version, which might be called the first-order polarization propagator approximation. The second-order polarization propagator approximation (SOPPA) [11], which provides correlated results of MP2 quality, has been developed for hyperpolarizabilities as well as linear polarizabilities [12].

Even for medium-size systems correlated calculations can be quite tedious. Thus, one may want to utilize a short-cut, even though some accuracy is lost. Assuming it is feasible to obtain the static correlated property, $P^{\text{corr}}(\text{static})$, an estimate of the dynamic (non-resonant) value can be made by scaling the static result according to

$$P^{\text{corr}}(\text{dynamic}) \simeq \frac{P^{\text{corr}}(\text{static})}{P^{\text{TDHF}}(\text{static})} P^{\text{TDHF}}(\text{dynamic}). \quad (2.18)$$

Another possibility, when correlated frequency-dependent values for just a single dynamic property are available, is to obtain an approximation for other dynamic properties using a power series expansion through fourth-order in the optical frequencies. Through that order just three parameters, at most, determine the frequency-dependence of *all* monochromatic NLO processes [13].

A time-dependent density functional theory (TDDFT) treatment, based on the Kohn-Sham method, may be carried out in a manner that is similar to TDHF. The major formal difference between the two lies in the replacement of the TDHF exchange contribution [second term in the double sum of Eq. (2.14)] by a term that involves the time-dependent exchange-correlation (XC) potential, V_{ij}^{XC} . The latter, in turn, depends upon the time-dependent density function, $\rho(x, t)$. The potential V^{XC} comes in many different variants. For sake of simplicity we consider here only generalized gradient approximations (GGAs). However, our formulation is readily

extended to meta-GGA and also to hybrid functionals using the TDHF expression for ‘exact’ exchange in Eq. (2.10).

From Eq. (2.15)

$$\rho = 2 \sum_{i=1}^{\text{occ}} \psi_i^* \psi_i = \sum_{kl} D_{kl} \chi_k^* \chi_l \quad (2.19)$$

and, for GGAs,

$$\nabla \rho = \sum_{kl} D_{kl} \nabla (\chi_k^* \chi_l) \quad (2.20)$$

where the superscript ⁽⁰⁾ on the density matrix has been dropped because perturbation corrections are now included. Hence, the density matrix and the density function are both time-dependent. In principle, V^{XC} should be obtained by taking the functional derivative of the XC action, A^{XC} , with respect to $\rho(r, t)$ [14], but in practice the adiabatic approximation is employed, in which case A^{XC} is replaced by the time-independent XC energy, E^{XC} . If we write

$$E^{\text{XC}} = \int f^{\text{XC}}(\rho, |\nabla \rho|^2) d\mathbf{x} \quad (2.21)$$

then, in the absence of any fields, it follows that the matrix elements of the XC potential in the basis set χ are given by

$$V_{ij}^{\text{XC}} = \int \left[\frac{\partial f^{\text{XC}}}{\partial \rho} \chi_i^* \chi_j + 2 \frac{\partial f^{\text{XC}}}{\partial |\nabla \rho|^2} \nabla \rho \cdot \nabla (\chi_i^* \chi_j) \right] d\mathbf{x} \quad (2.22)$$

as Pople et al. have shown using integration by parts [15].

The next step is to expand the integrand as a power series in the field(s). Thus, in first-order, applying the chain rule to the $\frac{\partial f^{\text{XC}}}{\partial \rho}$ term gives rise to two contributions one of which is $\frac{\partial^2 f^{\text{XC}}}{\partial \rho^2} \frac{d\rho}{dE_{\pm\omega}} \Big|_{E_{\pm\omega}=0}$. According to the adiabatic approximation $\frac{\partial^2 f^{\text{XC}}}{\partial \rho^2}$ is evaluated as if the field were static. The other contribution arises from the derivative of $\frac{\partial f^{\text{XC}}}{\partial \rho}$ with respect to $|\nabla \rho|^2$ evaluated, again, in the adiabatic approximation. There are likewise two first-order contributions that occur when the chain rule is applied to the second term in Eq. (2.22) plus a contribution from the derivative with respect to $E_{\pm\omega}$ of the factor $\nabla \rho(x, t)$ appearing in that term. Thus, there are a total of five terms involving first and second derivatives of f^{XC} needed for the first-order perturbation equation. An explicit expression for static fields, that may be easily generalized for the time-dependent case, is given in Ref. [16]. In second-order one also needs third derivatives and the expressions become much messier (see [17]). Nonetheless, an automatic procedure for determining the required derivatives is available [18, 19]. Of course, the integration in Eq. (2.22) must be carried out numerically just as in ordinary field-free DFT.

Besides the field-dependent XC potential one must also evaluate derivatives of the potential (with respect to ρ and $|\nabla\rho|^2$) in order to obtain the complete XC contribution to the first and second hyperpolarizability. However, the $2n + 1$ rule is maintained. Again, the required expressions have been reported for static fields [16, 17] and, as noted above, the higher-order functional derivatives of f^{XC} can be determined automatically.

We have focused here on the formal aspects of TDDFT. The efficiency of any particular implementation will depend upon the computational strategy employed, especially with regard to the method of integration (grid-based or not) and whether density fitting is used. The advantage of density fitting for the polarizability of large molecules in static fields has been demonstrated [20].

In addition to the perturbation theory procedure, there is also the possibility of calculating frequency-dependent electronic (hyper)polarizabilities numerically through DFT molecular dynamics simulations. At the present time this approach remains to be fully explored.

2.4 Solving the TDHF and TDDFT Equations

The previous section contains an overview of the time-dependent Hartree-Fock (TDHF) and time-dependent DFT [or more precisely, time-dependent Kohn-Sham (TDKS)] perturbation theory methods. In this section we present explicit expressions for the perturbation equations and their solutions, which in general terms is the same in either case. For that purpose it is convenient to use the compact notation illustrated below for the Fock Hamiltonian matrix:

$$\begin{aligned} \underline{\underline{F}} &= \underline{\underline{F}}^{(0)} + \sum_{\zeta} \underline{\underline{F}}_{\zeta}^{(1)} E_{\zeta} + \sum_{\zeta\eta} \underline{\underline{F}}_{\zeta\eta}^{(2)} E_{\zeta} E_{\eta} + \sum_{\zeta\eta\kappa} \underline{\underline{F}}_{\zeta\eta\kappa}^{(3)} E_{\zeta} E_{\eta} E_{\kappa} + \cdots \\ &\rightarrow F + \sum_{\zeta} F_{\zeta} E_{\zeta} + \sum_{\zeta\eta} F_{\zeta\eta} E_{\zeta} E_{\eta} + \sum_{\zeta\eta\kappa} F_{\zeta\eta\kappa} E_{\zeta} E_{\eta} E_{\kappa} + \cdots \end{aligned} \quad (2.23)$$

Note that the double underline to indicate a matrix is now omitted and the number of indices for the Cartesian directions $\zeta, \eta, \dots$ gives the order of perturbation theory. The field-free matrix F is given by Eq. (2.14); F_{ζ} is obtained from the same equation by replacing $\hat{h}(1)$ with $-\hat{\mu}_{\zeta}(1)$ and $D^{(0)}$ with D_{ζ} ; and finally, $F_{\zeta\eta}, F_{\zeta\eta\kappa}$, etc. are obtained for TDHF by deleting the $\hat{h}^{(1)}$ term in Eq. (2.14) and replacing $D^{(0)}$ with $D_{\zeta\eta}, D_{\zeta\eta\kappa}$, etc. For TDKS the Fock matrices are different, but can be determined as described in the previous section. The field frequencies are not shown in Eq. (2.23). They are, however, included later on. As before, we assume that the molecular orbitals are restricted to double occupancy so that there is no spin polarization. Finally, for a more detailed presentation of this notation and the following discussion we recommend Ref. [9].

Table 2.1 TDHF/TDKS perturbation equations and normalization conditions

Order	Perturbation equations	Normalization conditions
0th	$FC = SC\varepsilon$	$C^\dagger SC = 1$
1st	$F_\zeta(\omega_1)C + FC_\zeta(\omega_1) + \omega_1 SC_\zeta(\omega_1)$ $= SC_\zeta(\omega_1)\varepsilon + SC\varepsilon_\zeta(\omega_1)$	$C^\dagger SC_\zeta(\omega_1) + C_\zeta^\dagger(-\omega_1)SC = 0$
2nd	$F_{\zeta\eta}(\omega_1, \omega_2)C + F_\zeta(\omega_1)C_\eta(\omega_2) + F_\eta(\omega_2)C_\zeta(\omega_1)$ $+ FC_{\zeta\eta}(\omega_1, \omega_2) + (\omega_1 + \omega_2)SC_{\zeta\eta}(\omega_1, \omega_2)$ $= SC_{\zeta\eta}(\omega_1, \omega_2)\varepsilon + SC_\zeta(\omega_1)\varepsilon_\eta(\omega_2)$ $+ SC_\eta(\omega_2)\varepsilon_\zeta(\omega_1) + SC\varepsilon_{\zeta\eta}(\omega_1, \omega_2)$	$C^\dagger SC_{\zeta\eta}(\omega_1, \omega_2)$ $+ C_\eta^\dagger(-\omega_2)SC_\zeta(\omega_1)$ $+ C_{\zeta\eta}^\dagger(-\omega_1, -\omega_2)SC$ $+ C_\zeta^\dagger(-\omega_1)SC_\eta(\omega_2) = 0$

Table 2.1 contains the TDHF/TDKS perturbation equations and normalization conditions through second-order, which is sufficient to calculate α , β and γ according to the $2n + 1$ rule. For many (but not all) NLO processes of interest ω_1 and ω_2 are equal to $\pm\omega$ ($\omega > 0$) or 0. In the same notation, the corresponding density matrices are

0th-order:

$$D = CnC^\dagger$$

1st-order:

$$D_\zeta(\omega_1) = C_\zeta(\omega_1)nC^\dagger + CnC_\zeta^\dagger(-\omega_1)$$

and 2nd-order:

$$D_{\zeta\eta}(\omega_1, \omega_2) = C_{\zeta\eta}(\omega_1, \omega_2)nC^\dagger + C_\eta(\omega_2)nC_\zeta^\dagger(-\omega_1) \\ + C_\zeta(\omega_1)nC_\eta^\dagger(-\omega_2) + CnC_{\zeta\eta}^\dagger(-\omega_1, -\omega_2). \quad (2.24)$$

These density matrices are, as usual, in the atomic orbital representation.

As shown by Karna and Dupuis [9], the perturbation theory equations can be solved by introducing a set of transformation matrices, U ,

$$C_\zeta(\omega_1) = CU_\zeta(\omega_1) \\ C_{\zeta\eta}(\omega_1, \omega_2) = CU_{\zeta\eta}(\omega_1, \omega_2), \quad (2.25)$$

as well as the G matrices,

$$G_\zeta(\omega_1) = C^\dagger F_\zeta(\omega_1)C \\ G_{\zeta\eta}(\omega_1, \omega_2) = C^\dagger F_{\zeta\eta}(\omega_1, \omega_2)C. \quad (2.26)$$

which are both represented in the molecular orbital basis. Multiplying the perturbation equations from the left by $C^\dagger$, one obtains relations that immediately yield the

Table 2.2 TDHF/TDKS Lagrange multiplier matrices

Order	Equation
0th	$\varepsilon = C^\dagger F C$
1st	$\varepsilon_\zeta(\omega_1) = G_\zeta(\omega_1) + \varepsilon U_\zeta(\omega_1) - U_\zeta(\omega_1)\varepsilon + \omega_1 U_\zeta(\omega_1)$
2nd	$\begin{aligned} \varepsilon_{\zeta\eta}(\omega_1, \omega_2) = & G_{\zeta\eta}(\omega_1, \omega_2) + G_\zeta(\omega_1)U_\eta(\omega_2) + G_\eta(\omega_2)U_\zeta(\omega_1) \\ & + \varepsilon U_{\zeta\eta}(\omega_1, \omega_2) - U_{\zeta\eta}(\omega_1, \omega_2)\varepsilon \\ & - U_\zeta(\omega_1)\varepsilon_\eta(\omega_2) - U_\eta(\omega_2)\varepsilon_\zeta(\omega_1) + (\omega_1 + \omega_2)U_{\zeta\eta}(\omega_1, \omega_2) \end{aligned}$

Lagrange multiplier matrices reported in Table 2.2. Then, the off-diagonal blocks of the U matrices (that connect the set of occupied orbitals with the set of unoccupied orbitals) are determined by the fact that the corresponding blocks of the Lagrange multiplier matrices (see Table 2.2) must vanish. The diagonal blocks of the U matrices are determined by the normalization conditions. Substitution of Eq. (2.24) into these conditions gives

$$\begin{aligned} U_\zeta(\omega_1) + U_\zeta^\dagger(-\omega_1) &= 0 \\ U_{\zeta\eta}(\omega_1, \omega_2) + U_\zeta^\dagger(-\omega_1)U_\eta(\omega_2) + U_\eta^\dagger(-\omega_2)U_\zeta(\omega_1) + U_{\zeta\eta}^\dagger(-\omega_1, -\omega_2) &= 0. \end{aligned} \quad (2.27)$$

For the non-canonical solution one makes the choice

$$\begin{aligned} U_\zeta(\omega_1) &= U_\zeta^\dagger(-\omega_1) \\ U_{\zeta\eta}(\omega_1, \omega_2) &= U_{\zeta\eta}^\dagger(-\omega_1, -\omega_2) \end{aligned} \quad (2.28)$$

which leads to the diagonal blocks of U in Table 2.3. The results shown are expressed in terms of T matrices also reported in the table.

From the solutions to the TDHF or TDKS equations one can directly obtain the $n + 1$ rule (hyper)polarizabilities for both static and dynamic fields. The polarizabilities are given by

$$\alpha_{\zeta\eta}(\mp\omega_1; \pm\omega_1) = -\text{Tr} [M_\zeta D_\eta(\pm\omega_1)], \quad (2.29)$$

Table 2.3 Solutions for the TDHF/TDKS coefficient matrices in terms of U [see Eq. (2.25)]

Matrix	1st order	2nd order
T-matrix		$\begin{aligned} T_{\zeta\eta}(\omega_1, \omega_2) = & G_\zeta(\omega_1)U_\eta(\omega_2) \\ & - U_\zeta(\omega_1)G_\eta(\omega_2) \\ & + G_\eta(\omega_2)U_\zeta(\omega_1) \\ & - U_\eta(\omega_2)G_\zeta(\omega_1) \end{aligned}$
U-matrix block diagonal elements	$U_\zeta(\omega_1) = 0$	$U_{\zeta\eta}(\omega_1, \omega_2) = \frac{1}{2} \times [U_\zeta(\omega_1)U_\eta(\omega_2) + U_\eta(\omega_2)U_\zeta(\omega_1)]$
U-matrix non-diagonal blocks	$\begin{aligned} U_{\zeta,ij}(\omega_1) \\ = \frac{G_{\zeta,ij}(\omega_1)}{\varepsilon_j - \varepsilon_i - \omega_1} \end{aligned}$	$\begin{aligned} U_{\zeta\eta,ij}(\omega_1, \omega_2) \\ = \frac{G_{\zeta\eta,ij}(\omega_1, \omega_2) + T_{\zeta\eta,ij}(\omega_1, \omega_2)}{\varepsilon_j - \varepsilon_i - (\omega_1 + \omega_2)} \end{aligned}$

where M_ζ is the ζ component of the dipole moment matrix in Eq. (2.17) and D_η is defined in Eq. (2.24). Similarly, the first hyperpolarizabilities can be expressed in terms of the second-order density matrices:

$$\beta_{\zeta\eta\kappa}(-\omega_1 - \omega_2; \omega_1, \omega_2) = -\text{Tr} [M_\zeta D_{\eta\kappa}(\omega_1, \omega_2)]. \quad (2.30)$$

and the second hyperpolarizabilities in terms of the third-order density matrices

$$\gamma_{\zeta\eta\kappa\lambda}(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3) = -\text{Tr} [M_\zeta D_{\eta\kappa\lambda}(\omega_1, \omega_2, \omega_3)]. \quad (2.31)$$

The conversion of Eqs. (2.30) and (2.31) into $2n + 1$ rule formulas requires a complicated sequence of steps that will not be presented here. A fairly compact general expression can be developed for the first hyperpolarizability. There are additional terms in TDKS that are not present in TDHF. These were discussed in the previous section where appropriate references were cited.

The analogous result for the second hyperpolarizability is much less compact. Explicit expressions for monochromatic processes, in the presence or absence of a static field may be found in Table VIII of Ref. [9]. Some of the more important second- and third-order NLO properties were described in Chap. 1 where a tabular summary (see Table 1.1) is also provided.

2.5 Vibrational Linear and Nonlinear Polarizabilities

The vibrational (hyper)polarizability is **not** the contribution due to zero-point vibrational averaging. That is a much smaller effect. In order to explain the origin of the vibrational hyperpolarizability we return to the SOS formulas for the electronic properties in Eqs. (2.7), (2.8) and (2.9). Those expressions were obtained using the pure electronic wavefunctions of Eq. (2.2) with the nuclei clamped at the equilibrium geometry $\mathbf{X}_0$. However, the complete Born-Oppenheimer (electric) field-free states are vibronic products of the form:

$$|K, k\rangle = \phi_K(\mathbf{X}; \mathbf{x}) \chi_k^K(\mathbf{X}) \quad (2.32)$$

where $\chi_k^K(\mathbf{X})$ is the solution of the vibrational Schrödinger equation

$$[\hat{T}_n(\mathbf{X}) + E_K(\mathbf{X})] \chi_k^K(\mathbf{X}) = E_k^K \chi_k^K(\mathbf{X}). \quad (2.33)$$

Note that all quantities in Eq. (2.33) are field-free even though the superscript $^{(0)}$ has been omitted. $\hat{T}_n$ is the vibrational kinetic energy operator; the electronic energy $E_K = E_K^{(0)}$ [cf. Eq. (2.2)] serves as the potential energy function for vibrational motion in electronic state $|K\rangle$; and $E_k^K = E_K(\mathbf{X}_0) + e_k^K$ is the total (vibronic) energy of state $|Kk\rangle$.

SOS expressions for the NLO properties in terms of the Born-Oppenheimer vibronic states may be derived simply by making the replacements $|K\rangle \rightarrow |K, k\rangle$ and $\omega_K \rightarrow \omega_{Kk} = E_k^K/\hbar$ in Eqs. (2.7), (2.8) and (2.9). Moreover, the prime on the summations should now be understood to omit just the vibronic ground state $|K = 0, k = 0\rangle$. It is important to note that the sums include all $|0, k\rangle$ with k unequal to zero, which correspond to excited vibrational states on the ground electronic state potential energy surface (PES). These are the terms that give rise to the vibrational (hyper)polarizability.

Let us consider the SOS expression for the linear polarizability [cf. Eq. (2.7)] in terms of vibronic states. After integration over electronic coordinates the dipole moment matrix element $\langle 0, 0 | \hat{\mu}_\zeta(\mathbf{x}, \mathbf{X}) | K = 0, k \rangle$ becomes $\langle 0 | \mu_\zeta^{K=0}(\mathbf{X}) | k \rangle$, where $\mu_\zeta^{K=0}(\mathbf{X})$ is the dipole moment function (ζ component) for electronic state $|K = 0\rangle$. The vibrational polarizability can, then, be written as

$$\alpha_{\zeta, \eta}^{\text{v}}(-\omega_\sigma; \omega_1) = \frac{1}{\hbar} \sum_{\sigma, 1} P_{-\sigma, 1} \sum_k' \frac{1}{\omega_k - \omega_\sigma} \langle 0 | \mu_\zeta(\mathbf{X}) | k \rangle \langle k | \mu_\eta(\mathbf{X}) | 0 \rangle \quad (2.34)$$

where, for convenience, the superscript $K = 0$ on μ has been omitted.

At this point it is convenient to introduce vibrational normal coordinates $\{Q_a\}$. This implies a transformation from the $3N$ displacement coordinates $\mathbf{X} - \mathbf{X}_0$ to $3N - 6Q_a$ plus three center-of-mass coordinates and three angles describing the molecular orientation (for linear molecules there are $3N - 5$ normal coordinates and two angles of orientation). Assuming small displacements about the equilibrium geometry, as well as fixed orientation (see more later) and center of mass, we may expand the dipole moment function in the power series:

$$\mu_\zeta(\mathbf{X}) = \mu_\zeta(\mathbf{X}_0) + \sum_a \left(\frac{\partial \mu_\zeta}{\partial Q_a} \right)_0 Q_a + \frac{1}{2} \sum_{a,b} \left(\frac{\partial^2 \mu_\zeta}{\partial Q_a \partial Q_b} \right)_0 Q_a Q_b + \dots, \quad (2.35)$$

with the sums running over all normal coordinates. Upon evaluation of the matrix elements in Eq. (2.34) by integration over normal coordinates, the contribution due to the constant term in Eq. (2.35) will vanish because the wavefunctions are orthogonal. Hence, the first term to consider is linear in the displacements. It may be referred to as the harmonic, or zeroth-order, electric dipole contribution. The term that is quadratic in the displacements is defined to be first-order in electric dipole anharmonicity, the cubic term is second-order, and so forth.

A similar expansion of the PES leads to vanishing first derivatives (due to the equilibrium condition at $\mathbf{X} = \mathbf{X}_0$):

$$\begin{aligned} E_{K=0}(\mathbf{X}) &= E_{K=0}(\mathbf{X}_0) + V_n(\mathbf{Q}) \\ V_n(\mathbf{Q}) &= \frac{1}{2} \sum_{a,b} \left(\frac{\partial^2 V_n}{\partial Q_a \partial Q_b} \right)_0 Q_a Q_b \\ &\quad + \frac{1}{6} \sum_{a,b,c} \left(\frac{\partial^3 V_n}{\partial Q_a \partial Q_b \partial Q_c} \right)_0 Q_a Q_b Q_c + \dots \end{aligned} \quad (2.36)$$

Thus, the quadratic terms constitute the mechanical zeroth-order (harmonic) approximation and the second derivatives are the harmonic (or quadratic) force constants. The cubic terms, involving cubic force constants, are first-order in mechanical anharmonicity, etc. The expansions in Eqs.(2.35) and (2.36) form the basis for the double (electrical, mechanical) perturbation theory treatment of vibrational (hyper)polarizabilities developed by Bishop and Kirtman [4, 21], hereafter referred to as BKPT. In BKPT the vibrational wavefunctions, $\chi_k(\mathbf{X})$, and vibrational energy levels, e_k , are found by ordinary Rayleigh-Schrödinger perturbation theory applied to the vibrational Schrödinger equation (2.33) using the potential energy function of Eq.(2.36) with the definition of orders given above (the $E_{K=0}(\mathbf{X}_0)$ term appears on both sides of Eq.(2.33) and cancels out).

Substituting the dipole moment and potential energy expansions into Eq.(2.34), and assuming that the frequency of the electric field is in the non-resonant region of the spectrum (below the lowest electronic transition), the result can be expressed as the perturbation series

$$\alpha^v(-\omega_\sigma; \omega) = [\mu^2] = [\mu^2]^0 + [\mu^2]^{\text{II}} + \dots \quad (2.37)$$

For sake of simplicity, the directional indices in Eq.(2.37) have been removed as well as the optical frequency on the right hand side. We have also avoided writing out the full expressions, which may be found in [4, 21]. The superscripts indicate the total order in mechanical and electrical anharmonicity as explained below. Our notation μ^2 indicates that the electrical factor in each term is a product of two dipole derivatives. The product $\frac{\partial \mu}{\partial Q_a} \frac{\partial \mu}{\partial Q_b}$ is zeroth-order in electrical anharmonicity, $\frac{\partial^2 \mu}{\partial Q_a \partial Q_b} \frac{\partial \mu}{\partial Q_c}$ is first-order, $\frac{\partial^2 \mu}{\partial Q_a \partial Q_b} \frac{\partial^2 \mu}{\partial Q_c \partial Q_d}$ (and $\frac{\partial^3 \mu}{\partial Q_a \partial Q_b \partial Q_c} \frac{\partial \mu}{\partial Q_d}$) is second-order, and so forth.

Each of the individual perturbation terms within the square brackets of Eq.(2.37) is the product of an electric dipole factor, as just described, multiplied by a mechanical factor that depends on the vibrational force constants. After carrying out the perturbation expansion, the mechanical factors contain an harmonic frequency in the denominator and anharmonic force constants in the numerator. In zeroth-order the mechanical factor in the numerator is unity [see Eq.(2.38) below]; in first-order the individual terms are linear in the cubic force constants; in second-order they are quadratic in the cubic force constants or linear in the quartic force constants, etc.

We have used superscripts on the square brackets to specify the total order of perturbation theory, which is the sum of the order in electrical anharmonicity, $n = 0, 1, \dots$ plus the order in mechanical anharmonicity, $m = 0, 1, \dots$. This means that the term of order II contains all contributions of order (n, m) such that $n + m = 2$. When the anharmonicity is small, the zeroth-order doubly harmonic approximation ($\omega_\sigma = \omega_1 = \omega$):

$$[\mu^2]^0 = \frac{1}{2} \sum_{\sigma} P_{\sigma,1} \sum_a \frac{\partial \mu_{\xi}}{\partial Q_a} \frac{\partial \mu_{\eta}}{\partial Q_a} \left(\frac{1}{\omega_a - \omega_{\sigma}} \right) \left(\frac{1}{\omega_a + \omega_{\sigma}} \right) \quad (2.38)$$

may be sufficient. Some manipulations, and the fact that the matrix elements of Q_a depend upon ω_a , are required to achieve the form of Eq. (2.38) (see [4]). Finally, we note that a symmetry rule prevents any odd order perturbation terms from occurring in Eq. (2.37).

Next we turn to the first hyperpolarizability. Reflecting on Eq. (2.8) one can see that there are three ways to generate the ground electronic state: (1) $K = 0, L \neq 0$; (2) $K \neq 0, L = 0$; and (3) $K = 0, L = 0$. For case (1) we neglect the vibrational energy associated with excited electronic state L as compared to the electronic excitation energy. Then the sum over L creates the linear polarizability. If the optical frequencies associated with the electric fields lie well below the first electronic transition the frequency-dependence of the linear polarizability may be neglected (see further discussion later). In that event, the analogue of Eq. (2.37) for case 1 is

$$\beta^v(-\omega_\sigma; \omega_1, \omega_2) = [\mu\alpha] = [\mu\alpha]^0 + [\mu\alpha]^{\text{II}} + \dots \quad \text{case (1)}. \quad (2.39)$$

In order to obtain this result both α and μ have been expanded as power series in the normal coordinates. The square bracket $[\mu\alpha]$ indicates that each term involves the product of a dipole derivative multiplied by a linear polarizability derivative. Using the same definition of orders as for the dipole expansion it turns out, again, that only even order terms appear in the perturbation series.

For case (2) identical considerations apply as for case (1). In fact, the contribution to the vibrational first hyperpolarizability is the same for both. That leaves $K = L = 0$, which gives rise to:

$$\beta^v(-\omega_\sigma; \omega_1, \omega_2) = [\mu^3] = [\mu^3]^{\text{I}} + [\mu^3]^{\text{III}} + \dots \quad \text{case (3)}. \quad (2.40)$$

At this point it should be obvious how to interpret the square brackets in Eq. (2.40).

Finally, we consider the second (hyper)polarizability [cf. Eq. (2.9)]. There are four different types of square bracket that occur. Their form and origin are shown below:

$$\begin{aligned} [\mu\beta]^0 + [\mu\beta]^{\text{II}} + \dots &\leftarrow \gamma^{(+)}(K = 0; M = 0) \\ [\alpha^2]^0 + [\alpha^2]^{\text{II}} + \dots &\leftarrow \gamma^{(+)}(L = 0) \\ [\mu^2\alpha]^{\text{I}} + [\mu^2\alpha]^{\text{III}} + \dots &\leftarrow \begin{cases} \gamma^{(+)}(K, L = 0; K, M = 0; L, M = 0) \\ \gamma^{(-)}(K = 0; L = 0) \end{cases} \\ [\mu^4]^{\text{II}} + [\mu^4]^{\text{IV}} + \dots &\leftarrow \gamma^{(+)}(K, L, M = 0); \gamma^{(-)}(K = 0; L = 0). \end{aligned} \quad (2.41)$$

Here $\gamma^{(+)}$ and $\gamma^{(-)}$ refer to the first and second terms in Eq. (2.9) respectively. The semi-colons inside the parentheses separate the different cases, which are identified by specifying the electronic indices that are zero (while the others take all values

except zero). The $[\mu^4]$ perturbation series begins at second-order because the zeroth-order terms from $\gamma^{(+)}$ and $\gamma^{(-)}$ cancel one another [22].

From Eqs. (2.35) and (2.36) it can be inferred that ab initio computations will rapidly become more time consuming as one proceeds to higher order in perturbation theory because of the occurrence of higher order derivatives, which are more difficult to obtain individually and more numerous. Even a double harmonic treatment can be tedious for a large molecule since all the harmonic force constants must be calculated. Thus, it is of value to have an alternative procedure that is computationally more efficient, even though some (reasonable) approximations may have to be introduced. The so-called finite field-nuclear relaxation (FF-NR) method fulfills that goal ([23], see also [24]). It has been successfully applied to many small-to-medium size molecules and, recently, to infinite periodic systems as well [25, 26]. Although there is a subsequent more advanced version (see later), the original method is, with one exception, equivalent to BKPT through first-order. In either procedure one obtains the leading term in the perturbation series for each type of square bracket. For the static γ^v , this means that a second-order $[\mu^4]^{\text{II}}$ term in Eq. (2.41) is also included. A limitation of the FF-NR method is that the L&NLO properties are determined only in those circumstances where all external fields are either static or near the high frequency limit. This covers several of the more important cases. A modification is required to treat DFWM [27].

The main step in the FF-NR procedure is geometry optimization in the presence of a finite (static) field. In the simpler (first-order) version this is followed by evaluation of the static electronic dipolar properties (μ^e, α^e, β^e) at the relaxed geometry. For good accuracy the geometry optimization should be done with tight thresholds. Most importantly, the molecule cannot be allowed to rotate (in this regard the field-free Eckart conditions must be satisfied [28]) so that the direction of the field with respect to molecular axes remains unchanged during geometry optimization. The effect of rotation may be taken into account by carrying out calculations for different field directions followed by classical orientational averaging [29].

Let P^e be a static electronic dipolar property and Q_E the optimized set of normal coordinate displacements in the presence of the finite field $\mathbf{E}$. Then, if $\Delta P^e = P^e(\mathbf{E}, Q_E) - P^e(\mathbf{E}, 0)$ is expanded as a power series in $\mathbf{E}$, the expansion coefficients can be simply related to the vibrational (hyper)polarizabilities at $Q = 0$, i.e.

$$\begin{aligned} (\Delta\mu_\zeta)_{Q_E} &= \sum_{\eta} a_1 E_\eta + \frac{1}{2} \sum_{\eta\kappa} b_1 E_\eta E_\kappa + \frac{1}{6} \sum_{\eta\kappa\lambda} g_1 E_\eta E_\kappa E_\lambda + \dots \\ (\Delta\alpha_{\zeta\eta})_{Q_E} &= \sum_{\kappa} b_2 E_\kappa + \frac{1}{2} \sum_{\kappa\lambda} g_2 E_\kappa E_\lambda + \dots \\ (\Delta\beta_{\zeta\eta\kappa})_{Q_E} &= \sum_{\lambda} g_3 E_\lambda \end{aligned} \quad (2.42)$$

with

$$\begin{aligned}
a_1 - \alpha^e(0) &= \alpha_{\zeta\eta}^{nr}(0; 0); & b_1 - \beta^e(0) &= \beta_{\zeta\eta\kappa}^{nr}(0; 0, 0); & g_1 - \gamma^e(0) &= \gamma_{\zeta\eta\kappa\lambda}^{nr}(0; 0, 0, 0) \\
b_2 - \beta^e(0) &= \beta_{\zeta\eta\kappa}^{nr}(-\omega; \omega, 0)|_{\omega \rightarrow \infty}; & g_2 - \gamma^e(0) &= \gamma_{\zeta\eta\kappa\lambda}^{nr}(-\omega; \omega, 0, 0)|_{\omega \rightarrow \infty} \\
g_3 - \gamma^e(0) &= \gamma_{\zeta\eta\kappa\lambda}^{nr}(-2\omega; \omega, \omega, 0)|_{\omega \rightarrow \infty}
\end{aligned} \tag{2.43}$$

and $\alpha^e(0)$, $\beta^e(0)$, $\gamma^e(0)$ equal to the static electronic α , β , γ . The superscript nr here refers to the first-order nuclear relaxation treatment. Although all calculations are done with static fields, the last two lines in Eq. (2.43) yield dynamic NLO properties—the subscript $\omega \rightarrow \infty$ implies the limiting high frequency value. This same value is obtained from BKPT if the quantity $\left(\frac{\omega_v}{\omega}\right)^2$, with ω_v equal to a fundamental vibrational frequency, is negligible compared to unity for all ω_v . Under the same approximation the nr contribution to second and third harmonic generation, namely $\beta_{\zeta\eta\kappa}^{nr}(-2\omega; \omega, \omega)$ and $\gamma_{\zeta\eta\kappa\lambda}^{nr}(-3\omega; \omega, \omega, \omega)$, is zero. In fact, as a general rule, the more static fields that define the process, the larger will be the nuclear relaxation contribution relative to the pure electronic term. This means, for example, that one would expect vibrations to be more important for $\gamma(-\omega; \omega, 0, 0)$ (dc-Kerr effect) than for $\gamma(-2\omega; \omega, \omega, 0)$ or $\beta(-\omega; \omega, 0)$. In fact, for dc-Kerr the vibrations may be more important than pure electronic motions and for static γ vibrational contributions are often dominant.

The intensity-dependent refractive index (IDRI) $\gamma(-\omega; \omega, \omega, -\omega)$, or degenerate four-wave mixing (DFWM), is a special case. It turns out that the vibrational contribution is quite important for this property because one of the frequencies occurs with a negative sign leading to a cancellation that effectively produces two static fields. As noted above the original FF-NR method is readily modified to calculate DFWM [27].

Closely related to the FF-NR procedure are methods based on what are known as field-induced coordinates (FICs) [30, 31]. These coordinates are determined by the optimized set of normal coordinate displacements Q_E , defined above. After expanding the latter as a power series in the field, the linear coefficients (see below) determine three first-order FICs, one for each Cartesian field direction. The quadratic coefficients yield the second-order FICs, of which there are six—one for each pair of field directions. Regardless of the size of the molecule these are the only (9) coordinates that are needed to obtain the first-order vibrational NLO properties. They can be found analytically as well, but the numerical procedure is more efficient for large molecules.

Next we write the first-order FIC (κ component) as

$$\bar{\chi}_1^\kappa = \sum_a (M_1^\kappa)_a Q_a, \tag{2.44}$$

where $(M_1^\kappa)_a$ is the linear coefficient in the expansion of $(Q_a)_E$, as a function of E , obtained by a numerical fit. Then, in terms of the $(M_1^\kappa)_a$ the nr EOPE, for example, becomes just

$$\beta_{\zeta\eta\kappa}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty} = \frac{1}{2} \frac{\partial \alpha_{\zeta\eta}}{\partial \bar{\chi}_1^{\kappa}} \sum_a (M_1^{\kappa})_a^2. \quad (2.45)$$

In Eq. (2.45) the derivative in front of the summation must be evaluated numerically as well. However, only a single derivative is involved rather than a separate derivative for each normal coordinate. Moreover, symmetry coordinates may be used everywhere, instead of normal coordinates, making it unnecessary to calculate the Hessian.

An expression similar to Eq. (2.45) can be written for $\gamma^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$ except that α is replaced by β on the right hand side and the factor of 1/2 is replaced by 1/6. In this case, as well as in Eq. (2.45), only the first-order FIC is needed because the anharmonic contributions to EFISHG vanish in the limit $\omega \rightarrow \infty$. The expressions for the remaining nr properties are somewhat more complicated, but similar simplifications occur. The static γ is the most difficult property to compute since both first- and second-order FICs contribute. Moreover, several anharmonicity parameters enter into the formulas. A complete set of expressions for static and dynamic vibrational properties is given in [30].

The FF-NR approach has been extended beyond the lowest-order square bracket terms of each type. In fact, a treatment that is exact in principle is available [24]. One simply replaces the electronic property values in Eq. (2.42) by their zero-point vibrational average (ZPVA). In practice, the accuracy obtained will depend upon the level of approximation used to compute the ZPVA. Although this procedure has been successfully applied to small molecules, and is currently moving forward, further developments are necessary before it can be applied to large systems. It is important to realize, however, that the resulting contributions can be quite significant in systems with low frequency, large amplitude vibrational modes. The possibility of treating just that limited subset of vibrations within a large system has begun to be explored [32].

In the FF-NR and BKPT methods the electronic transition frequencies are assumed to be much larger than the frequencies of the (external) laser optical fields. Hansen et al. [33] have developed a response theory formulation that accounts for the vibrational contribution which is thereby omitted. This so-called ‘mixed’ term is difficult to compute, but could sometimes be important. Nonetheless, it is zero both in the static limit and in the ‘infinite’ optical frequency limit previously defined [34]. Initial calculations carried out by Hansen et al. [33] found the mixed term to be small.

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