

# Distributed first and second order hyperpolarizabilities: An improved calculation of nonlinear optical susceptibilities of molecular crystals

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The method of calculating distributed polarizabilities is extended to the first and second dipole hyperpolarizabilities, in order to describe more accurately the molecular response to strong and inhomogeneous external time-dependent electric fields. The dipolar response is expressed in terms of both potential related charge-density response functions and electric field related dipole-density response functions. The macroscopic linear, quadratic, and cubic optical dipole susceptibilities of molecular crystals are expressed in terms of the distributed (hyper) polarizabilities. This formulation differs from previous theories using distributed dipoles in that it allows for a rigorous treatment of both local induced dipoles and charge flow between different regions of the molecule. As an example, the distributed polarizabilities and first hyperpolarizabilities of urea at the self-consistent-field level are used to calculate the linear and quadratic susceptibilities of the urea crystal. The linear susceptibility does not differ substantially from that calculated with previous less rigorous models for distributed response, but the quadratic susceptibility is about 50% of that calculated with previous models. This indicates that the present treatment of distributed response should give a quadratic susceptibility in good agreement with experimental data, once the effects of electronic correlation, frequency dispersion, and the permanent crystal field are taken into account.  
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## I. INTRODUCTION

Quantitative understanding of the nonlinear optical response of molecular crystals and other molecular materials is desirable for systematic development of optimized molecular materials for nonlinear optics (NLO). Central to such understanding is the molecular hyperpolarizability. Improvements in computing power and advances in techniques of quantum chemistry have provided valuable insights into the factors that influence the hyperpolarizabilities of different molecules. Studies of frequency dependence also inform about work on resonance enhancement and re-absorption in NLO.

However, much of this work has been performed on isolated molecules in uniform electric fields, which afford only a first approximation to molecules in the material environment. In particular, the molecules are subject to large and strongly varying electric fields caused by the permanent charge distributions of the surrounding molecules, and to local electric fields caused by electric moments induced on the surrounding molecules by the external field. Furthermore, the response is not local within each molecule but involves contributions from flow of charge between different regions. The total molecular response depends on the pattern of fields ap-

plied, and the same total response in a uniform field can give different responses in nonuniform fields, depending on how it is distributed in space, as shown by calculations of linear response for model Langmuir-Blodgett films.<sup>1</sup> This situation is analogous to that in tomography, where nonuniform fields are used to obtain information about the distribution of response in the material under study.

We have therefore sought to calculate the distributed hyperpolarizability by extending Stone's treatment of the distributed polarizability.<sup>2</sup> In Stone's treatment the molecular charge distribution is expanded in a multicentered multipolar series around (atomic) sites and one considers the changes in the site multipoles that are caused by changes in the external potential. The induced molecular multipole moments of a given order can be exactly reproduced from the distributed contributions of the same order and from those of all lower orders. In particular, the usual dipole polarizability contains contributions from charge flow between basins. Nonlocal distributed hyperpolarizabilities are needed for a rigorous treatment not only of NLO<sup>3</sup> but also of other properties.<sup>4</sup>

One technical problem that arises is that relating changes of charge distribution to changes of potential, while convenient for calculations of interaction energies, does not yield

the response coefficients customarily used in nonlinear optics. These relate changes of multipole moment to changes of electric and magnetic fields (both of which must be present in an electromagnetic wave). This problem is resolved by a suitable choice of gauge. We therefore derive sets of hyperpolarizabilities in both schemes, in order to provide input suitable for interaction energies as well as for nonlinear optics.

Once the distributed hyperpolarizability is obtained, it must be incorporated into a suitable theory for the material response. Theories have been developed for molecular crystals<sup>5</sup> and for ordered Langmuir–Blodgett films.<sup>6</sup> These go beyond the point-dipole approximation to allow for distributed dipoles. However, they do not allow for the distributed charges necessary to treat charge flow between atomic basins, as described by the distributed response coefficients. Hence it is necessary to generalize the previous treatments to incorporate not only induced dipoles but also induced charges in each basin, both of which contribute to the internal electric fields and to the macroscopic polarization from which the nonlinear optical susceptibilities follow. This is done for the case of a molecular crystal, where suitable redefinitions allow results to be obtained that are similar in algebraic form to those obtained previously for dipoles alone.

## II. THEORY

### A. The distributed (hyper)polarizabilities of a molecule

Consider an isolated molecule interacting with an electromagnetic field. In the semiclassical approach the field is not quantized and can be characterized by the electrical potential  $\phi(\underline{r}, t)$  and the vector potential  $\underline{A}(\underline{r}, t)$ , obeying the Maxwell equations, while the molecule is described by the methods of quantum mechanics. The Hamiltonian of the system can be written as  $H(t) = H_0 + V(t)$ , where  $H_0$  is the Hamiltonian of the unperturbed molecule, with eigenfunctions  $|j\rangle$ , and  $V(t)$  is the time-dependent interaction or perturbation term:

$$V(t) = \sum_{i=1}^N \left[ \frac{q_i}{2m_i} (\underline{A}(\underline{r}_i, t) \cdot \underline{p}_i + \underline{p}_i \cdot \underline{A}(\underline{r}_i, t)) + \frac{q_i^2}{2m_i} \underline{A}(\underline{r}_i, t)^2 - q_i \phi(\underline{r}_i, t) \right], \quad (1)$$

where  $q_i, m_i, \underline{r}_i, \underline{p}_i$  are the charge, mass, space coordinates, and canonical momentum of the  $i$ th particle of the molecule. Interaction effects with spin have been neglected.

We are interested in the induced molecular dipole moment  $\underline{p}(t)$ , which is given by

$$\underline{p}(t) = \int d^3r \underline{r} \langle \psi_g(t) | \hat{\rho}(\underline{r}, t) | \psi_g(t) \rangle - \underline{p}_0, \quad (2)$$

where  $\psi_g(t)$  is the perturbed ground state wave function,  $\hat{\rho}(\underline{r}, t)$  is the molecular charge density operator

$$\hat{\rho}(\underline{r}) = \sum_{i=1}^N q_i \delta(\underline{r} - \underline{r}_i), \quad (3)$$

and  $\underline{p}_0$  is the permanent molecular dipole moment.

Using time-dependent perturbation theory, Orr and Ward<sup>7</sup> worked out a solution for the Fourier components of  $\underline{p}(t)$  up to third order in the perturbation, i.e.,

$$\underline{p}(\omega) = \underline{p}^{(1)}(\omega) + \underline{p}^{(2)}(\omega) + \underline{p}^{(3)}(\omega). \quad (4)$$

Particular terms  $\underline{p}^{(i)}(\omega)$  ( $i=1,2,3$ ), are characterized by the frequencies involved and the dependence on the perturbation, e.g., for a third-order process

$$\underline{p}^{(3)}(\omega) \propto V(\omega_1)V(\omega_2)V(\omega_3), \quad (5)$$

$$\omega = \omega_1 + \omega_2 + \omega_3, \quad (6)$$

where  $V(\omega)$  denotes a Fourier component of the perturbation  $V(t)$ . The equations for the  $\underline{p}^{(i)}(\omega)$  are

$$\underline{p}^{(1)}(\omega) = -I([\underline{p}, -\omega], [V, \omega]) \frac{1}{\hbar} \sum_{j \neq 0} \frac{\langle \underline{p} \rangle_{0j} \langle V^\omega \rangle_{j0}}{\omega_{j0} - \omega}, \quad (7)$$

$$\begin{aligned} \underline{p}^{(2)}(\omega) = & K_{-\omega, \omega_1, \omega_2} \frac{1}{2\hbar^2} I([\underline{p}, -\omega], [\bar{V}, \omega_1], [V, \omega_2]) \\ & \times \sum_{j, k \neq 0} \frac{\langle \underline{p} \rangle_{0j} \langle \bar{V}^{\omega_1} \rangle_{jk} \langle V^{\omega_2} \rangle_{k0}}{(\omega_{j0} - \omega)(\omega_{k0} - \omega_2)}, \end{aligned} \quad (8)$$

$$\begin{aligned} \underline{p}^{(3)}(\omega) = & -K_{-\omega, \omega_1, \omega_2, \omega_3} \\ & \times \frac{1}{6\hbar^3} I([\underline{p}, -\omega], [\bar{V}, \omega_1], [\bar{V}, \omega_2], [V, \omega_3]) \\ & \times \left[ \sum_{j, k, l \neq 0} \frac{\langle \underline{p} \rangle_{0j} \langle \bar{V}^{\omega_1} \rangle_{jk} \langle \bar{V}^{\omega_2} \rangle_{kl} \langle V^{\omega_3} \rangle_{l0}}{(\omega_{j0} - \omega)(\omega_{k0} - \omega_2 - \omega_3)(\omega_{l0} - \omega_3)} \right. \\ & \left. - \sum_{k, l \neq 0} \frac{\langle \underline{p} \rangle_{0k} \langle V^{\omega_1} \rangle_{k0} \langle V^{\omega_2} \rangle_{0l} \langle V^{\omega_3} \rangle_{l0}}{(\omega_{k0} - \omega)(\omega_{l0} - \omega_3)(\omega_{l0} + \omega_2)} \right], \end{aligned} \quad (9)$$

where  $\langle V^\omega \rangle_{jk} = \langle j | V(\omega) | k \rangle$ ,  $\langle \bar{V} \rangle_{mn} = \langle V \rangle_{mn} - \delta_{mn} \langle V \rangle_{00}$ , and  $\omega_{m0} = (E_m - E_0)/\hbar$ . The operator  $I([a, \omega_a], [b, \omega_b], \dots)$  generates additional terms by permuting the quantities  $a, b, \dots$ , together with the frequencies  $\omega_a, \omega_b, \dots$  in all possible ways, and the  $K_{-\omega, \omega_1, \omega_2, \dots}$  denote numerical factors depending on the number of zero and repeated frequencies in the set  $\omega_1, \omega_2, \dots$ . The values of  $K$  for different processes are given in the Appendix of Ref. 7. Damping effects have been neglected in Eqs. (7)–(9), which means that the frequencies of the external fields should be far away from any resonance.

The derivation is not restricted to the electric dipole polarization, but is equally suited for the calculation of electric polarizations of higher multipolar order and for magnetic polarization as well, by using the respective operators instead of the electric dipole operator  $\underline{p}$ .

In order to introduce the distribution scheme, the volume  $\Omega$  occupied by the molecule is partitioned, in a way yet to be specified, into  $n_s$  disjoint volumes  $\Omega_s$ , with no voids, so that  $\Omega = \sum_{s=1}^{n_s} \Omega_s$ . The potentials  $\underline{A}(\underline{r}, t)$  and  $\phi(\underline{r}, t)$  inside each partial volume can be expanded around an interior point  $\underline{r}_s$ :

$$\phi(\underline{r}, t) = \sum_s G_s(\underline{r}) \sum_{n=0}^{\infty} \frac{1}{n!} [\underline{r} - \underline{r}_s]^{[n]} [n] \nabla^{[n]} \phi(\underline{r}_s, t), \quad (10)$$

$$\underline{A}(\underline{r}, t) = \sum_s G_s(\underline{r}) \sum_{n=0}^{\infty} \frac{1}{n!} [\underline{r} - \underline{r}_s]^{[n]} [n] \nabla^{[n]} \underline{A}(\underline{r}_s, t), \quad (11)$$

where the expression  $a^{[n]}$  indicates an  $n$ -fold tensor (outer product) of the vector quantity  $a$ , and  $[n]$  denotes an  $n$ -fold tensor contraction. The quantity

$$G_s(\underline{r}) = 1 \quad \text{if } \underline{r} \text{ lies in } \Omega_s \\ = 0 \quad \text{otherwise} \quad (12)$$

and hence picks out values of  $\underline{r}$  that lie inside the chosen volume  $\Omega_s$ .

The interaction between molecules and electromagnetic radiation may also be expressed in terms of the magnetic and electric fields  $\underline{B}(\underline{r}, t)$  and  $\underline{E}(\underline{r}, t)$ , respectively, instead of the potentials. The connection between the fields and the potentials is given by

$$\underline{E} = -\nabla\phi - \frac{\partial \underline{A}}{\partial t}, \quad (13)$$

$$\underline{B} = \nabla \otimes \underline{A}. \quad (14)$$

There is freedom in the choice of the potentials, as the gauge transformation of the potentials  $\phi' = \phi - \partial f / \partial t, \underline{A}' = \underline{A} + \nabla f$ , where  $f(\underline{r}, t)$  is the gauge function, does not change the fields  $\underline{E}$  and  $\underline{B}$ . A convenient gauge for our purpose uses the transformation considered by Bloch,<sup>8</sup> in the form used by Lazzaretti,<sup>9</sup> and implicitly by Barron and Gray.<sup>10</sup> Here, the expansions of the potentials in Eqs. (10) and (11) are compared with the corresponding Taylor series for the electric and magnetic fields. The original treatment was restricted to a single expansion center  $\underline{r}_0$ , which is taken to be the origin, and must be generalized to a multicenter expansion at the centers  $\underline{r}_s$ . Choosing the gauge function  $f$  as

$$f^B(\underline{r}, t) = -\sum_s G_s(\underline{r}) \sum_{n=1}^{\infty} \frac{1}{n!} \nabla^{[n-1]} \underline{A}(\underline{r}_s, t) \\ [n][\underline{r} - \underline{r}_s]^{[n]} \quad (15)$$

leads, by using Eqs. (13) and (14) with the corresponding expansions of  $\underline{E}(\underline{r}, t)$  and  $\underline{B}(\underline{r}, t)$ , to the generalized Bloch potentials:

$$\phi^B(\underline{r}, t) = \phi(\underline{r}_0, t) + \sum_s G_s(\underline{r}) \sum_{n=1}^{\infty} \frac{1}{n!} \nabla^{[n-1]} \underline{E}(\underline{r}_s, t) \\ [n]([\underline{r} - \underline{r}_s]^{[n]} - [\underline{r} - \underline{r}_s]^{[n]}), \quad (16)$$

$$\underline{A}^B(\underline{r}, t) = \sum_s G_s(\underline{r}) \sum_{n=0}^{\infty} \frac{n+1}{(n+2)!} [\nabla^{[n]} \underline{B}(\underline{r}_s, t) \\ \otimes (\underline{r} - \underline{r}_s)][n][\underline{r} - \underline{r}_s]^{[n]}, \quad (17)$$

where  $\phi(\underline{r}_0, t)$  is the potential at the molecular origin  $\underline{r}_0 = (0, 0, 0)$ . For the derivation of Eq. (16) we used the following expression for the first expansion term of Eq. (10),  $\phi(\underline{r}_s, t)$ :

$$\phi(\underline{r}_s, t) = \phi(\underline{r}_0, t) + \sum_{n=1}^{\infty} \frac{1}{n!} [\underline{r} - \underline{r}_s]^{[n]} [n] \nabla^{[n-1]} \underline{E}(\underline{r}_s, t). \quad (18)$$

This equation is proved in Appendix A. Due to the freedom of choice for the point of origin of the potential,  $\phi(\underline{r}_0, t)$  can be set to zero for an isolated molecule, but has to be retained in general, e.g., if intermolecular interactions are considered.

According to Eqs. (16) and (17), in the Bloch gauge the vector potential  $\underline{A}^B$  is determined solely by the magnetic fields  $\underline{B}$  while  $\phi^B$  depends only on the electric field  $\underline{E}$ . This simplifies the separate treatment of magnetic and electric effects and contrasts with other gauge transformations like the Coulomb gauge, where  $\nabla\phi = 0$  *in vacuo* and  $\underline{A}$  depends both on  $\underline{E}$  and  $\underline{B}$ . The Coulomb gauge has often been used, for example, by Maaskant and Oosterhoff<sup>11</sup> for the calculation of polarizabilities and hyperpolarizabilities that occur in the theory of optical rotatory power. In the following, we will restrict ourselves to the treatment of the electric interactions, but the magnetic effects can essentially be treated along the same lines, taking into account that the term quadratic in  $\underline{A}$  has to be treated as a second-order perturbation term.

In the approximation considered, the Fourier components of the induced dipole moment  $\underline{p}(\omega)$  can generally be expressed by nonlocal (hyper)polarizability densities with respect to the Fourier components of the potentials:

$$\underline{p}(\omega) = \int d^3r \int d^3r' \alpha^\phi(\underline{r}, -\omega; \underline{r}', \omega) \phi(\underline{r}', \omega) + \frac{1}{2} \int d^3r \int d^3r' \int d^3r'' K_{-\omega, \omega_1, \omega_2} \\ \times \underline{\beta}^\phi(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2) \phi(\underline{r}', \omega_1) \phi(\underline{r}'', \omega_2) + \frac{1}{6} \int d^3r \int d^3r' \int d^3r'' \int d^3r''' \\ \times K_{-\omega, \omega_1, \omega_2, \omega_3} \underline{\gamma}^\phi(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2, \underline{r}''', \omega_3) \phi(\underline{r}', \omega_1) \phi(\underline{r}'', \omega_2) \phi(\underline{r}''', \omega_3), \quad (19)$$

where the polarization density response functions  $\alpha^\phi(\underline{r}, -\omega; \underline{r}', \omega)$ ,  $\underline{\beta}^\phi(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2)$ , and  $\underline{\gamma}^\phi(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2, \underline{r}''', \omega_3)$  are the polarizability, first hyperpolarizability, and second hyperpolarizability densities, respectively, which describe the response of the molecular charge distribution to applied external potentials.

More customarily,  $\underline{p}(\omega)$  is expressed by response functions with respect to the fields<sup>4</sup>

$$\begin{aligned}
\underline{p}(\omega) = & \int d^3r \int d^3r' \underline{\alpha}^E(\underline{r}, -\omega; \underline{r}', \omega) \cdot \underline{E}(\underline{r}', \omega) + \frac{1}{2} \int d^3r \int d^3r' \int d^3r'' K_{-\omega, \omega_1, \omega_2} \\
& \times \underline{\beta}^E(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2) : \underline{E}(\underline{r}'', \omega_2) \underline{E}(\underline{r}', \omega_1) + \frac{1}{6} \int d^3r \int d^3r' \int d^3r'' \int d^3r''' \\
& \times K_{-\omega, \omega_1, \omega_2, \omega_3} \underline{\gamma}^E(\underline{r}, -\omega; \underline{r}', \omega_1, \underline{r}'', \omega_2, \underline{r}''', \omega_3) : \underline{E}(\underline{r}''', \omega_3) \underline{E}(\underline{r}'', \omega_2) \underline{E}(\underline{r}', \omega_1). \quad (20)
\end{aligned}$$

Note that in treatments of nonlinear optics in molecular materials, the numerical factors in these two equations are often omitted, leading to the so-called perturbation series convention or *B* convention.<sup>12</sup>

With Eqs. (10) and (16), the matrix elements  $\langle V^\omega \rangle_{jk} = \int d^3r \phi(\underline{r}, \omega) \langle j | \hat{\rho}(\underline{r}) | k \rangle$  that occur in Eqs. (7)–(9) for a neutral molecule can be written in the distributed scheme in terms of the potential or in terms of the fields as

$$\langle V^\omega \rangle_{jk} = \sum_s \sum_{n=0}^{\infty} \frac{1}{n!} \langle M_s^{[n]} \rangle_{jk} [n] \underline{\nabla}^{[n]} \phi(\underline{r}_s, \omega) \quad (21)$$

$$\begin{aligned}
& = \sum_s \sum_{n=1}^{\infty} \frac{1}{n!} [(-\underline{r}_s)^{[n]} \langle q_s \rangle_{jk} - \langle M_s^{[n]} \rangle_{jk}] \\
& [n] \underline{\nabla}^{[n-1]} \underline{E}(\underline{r}_s, \omega), \quad (22)
\end{aligned}$$

where the distributed moment matrix elements  $\langle M_s^{[n]} \rangle_{jk}$  are defined by

$$\begin{aligned}
\langle M_s^{[n]} \rangle_{jk} & = \int d^3r G_s(\underline{r}) (\underline{r} - \underline{r}_s)^{[n]} \langle j | \hat{\rho}(\underline{r}) | k \rangle \\
& = \langle j | \sum_i G_s(\underline{r}_i) q_i (\underline{r}_i - \underline{r}_s)^{[n]} | k \rangle. \quad (23)
\end{aligned}$$

We use the symbols  $\langle q_s \rangle_{jk} \doteq \langle M_s^{[0]} \rangle_{jk}$ ,  $\langle \underline{\mu}_s \rangle_{jk} \doteq \langle M_s^{[1]} \rangle_{jk}$  for the (transition or permanent) moments of charge and dipole, respectively, in volume  $\Omega_s$ .

The matrix elements  $\langle \underline{p} \rangle_{jk}$  can be expressed in terms of the distributed moments as

$$\begin{aligned}
\langle \underline{p} \rangle_{jk} & = \int d^3r \sum_s G_s(\underline{r}) [\underline{r}_s + (\underline{r} - \underline{r}_s)] \langle j | \hat{\rho}(\underline{r}) | k \rangle \\
& = \sum_s (\underline{r}_s \langle q_s \rangle_{jk} + \langle \underline{\mu}_s \rangle_{jk}). \quad (24)
\end{aligned}$$

This is the generalization of a statement made by Stone<sup>2</sup> that the (induced or permanent) molecular dipole moment  $\underline{p}$  is the sum of distributed charge and dipole terms:

$$\underline{p} = \sum_s (\underline{r}_s q_s + \underline{\mu}_s). \quad (25)$$

With Eqs. (24) and (21) the  $\underline{p}^{(i)}(\omega)$  ( $i=1,2,3$ ) of Eqs. (7)–(9) can be expressed as

$$\begin{aligned}
\underline{p}^{(1)}(\omega) & = - \sum_{n=0}^{\infty} \sum_{ss'} [r_s \alpha_{ss'}^{0n}(-\omega; \omega) + \alpha_{ss'}^{1n}(-\omega; \omega)] \\
& [n] \underline{\nabla}^{[n]} \phi(\underline{r}_{s'}, \omega), \quad (26)
\end{aligned}$$

$$\begin{aligned}
\underline{p}^{(2)}(\omega) & = \frac{1}{2} K_{-\omega, \omega_1, \omega_2} \sum_{n_1, n_2=0}^{\infty} \sum_{ss's''} [r_s \beta_{ss's''}^{0n_1 n_2}(-\omega; \omega_1, \omega_2) \\
& + \beta_{ss's''}^{1n_1 n_2}(-\omega; \omega_1, \omega_2)] \\
& [n_1 + n_2] \underline{\nabla}^{[n_2]} \phi(\underline{r}_{s''}, \omega_2) \underline{\nabla}^{[n_1]} \phi(\underline{r}_{s'}, \omega_1), \quad (27)
\end{aligned}$$

$$\begin{aligned}
\underline{p}^{(3)}(\omega) & = - \frac{1}{6} K_{-\omega, \omega_1, \omega_2, \omega_3} \sum_{n_1, n_2, n_3=0}^{\infty} \sum_{ss's''s'''} [r_s \\
& \gamma_{ss's''s'''}^{0n_1 n_2 n_3}(-\omega; \omega_1, \omega_2, \omega_3) \\
& + \gamma_{ss's''s'''}^{1n_1 n_2 n_3}(-\omega; \omega_1, \omega_2, \omega_3)] [n_1 + n_2 + n_3] \\
& \underline{\nabla}^{[n_3]} \phi(\underline{r}_{s'''}, \omega_3) \\
& \underline{\nabla}^{[n_2]} \phi(\underline{r}_{s''}, \omega_2) \underline{\nabla}^{[n_1]} \phi(\underline{r}_{s'}, \omega_1), \quad (28)
\end{aligned}$$

where the distributed polarizabilities and hyperpolarizabilities are given by

$$\begin{aligned}
\alpha_{ss'}^{in}(-\omega; \omega) & = \frac{1}{\hbar} I([M_s^{[i]}, -\omega], [M_{s'}^{[n]}, \omega]) \\
& \sum_{j \neq 0} \frac{\langle M_s^{[i]} \rangle_{0j} \langle M_{s'}^{[n]} \rangle_{0j}}{\omega_{j0} - \omega}, \quad (29)
\end{aligned}$$

$$\begin{aligned}
\beta_{ss's''}^{in_1 n_2}(-\omega; \omega_1, \omega_2) & = \frac{1}{\hbar^2} I([M_s^{[i]}, -\omega], [\bar{M}_{s'}^{[n_1]}, \omega_1], [M_{s''}^{[n_2]}, \omega_2]) \\
& \sum_{j, k \neq 0} \frac{\langle M_s^{[i]} \rangle_{0j} \langle \bar{M}_{s'}^{[n_1]} \rangle_{jk} \langle M_{s''}^{[n_2]} \rangle_{k0}}{(\omega_{j0} - \omega)(\omega_{k0} - \omega_2)}, \quad (30)
\end{aligned}$$

$$\begin{aligned}
\gamma_{ss's''s'''}^{in_1 n_2 n_3}(-\omega; \omega_1, \omega_2, \omega_3) & = \frac{1}{\hbar^3} I([M_s^{[i]}, -\omega], [\bar{M}_{s'}^{[n_1]}, \omega_1], [\bar{M}_{s''}^{[n_2]}, \omega_2], [M_{s'''}^{[n_3]}, \omega_3]) \\
& \left[ \sum_{j, k, l \neq 0} \frac{\langle M_s^{[i]} \rangle_{0j} \langle \bar{M}_{s'}^{[n_1]} \rangle_{jk} \langle \bar{M}_{s''}^{[n_2]} \rangle_{kl} \langle M_{s'''}^{[n_3]} \rangle_{l0}}{(\omega_{j0} - \omega)(\omega_{k0} - \omega_2 - \omega_3)(\omega_{l0} - \omega_3)} \right. \\
& \left. - \sum_{j, k \neq 0} \frac{\langle M_s^{[i]} \rangle_{0k} \langle M_{s'}^{[n_1]} \rangle_{k0} \langle M_{s''}^{[n_2]} \rangle_{0l} \langle M_{s'''}^{[n_3]} \rangle_{l0}}{(\omega_{k0} - \omega)(\omega_{l0} - \omega_3)(\omega_{l0} + \omega_2)} \right]. \quad (31)
\end{aligned}$$

In terms of the electric fields and their gradients, we find

$$\underline{p}^{(1)}(\omega) = \sum_{n=1}^{\infty} \sum_{s's'} [r_s \alpha_{s's'}^{qn}(-\omega; \omega) + \alpha_{s's'}^{\mu n}(-\omega; \omega)] [n] \nabla^{[n-1]} \underline{E}(r_{s'}, \omega), \quad (32)$$

$$\underline{p}^{(2)}(\omega) = \frac{1}{2} K_{-\omega, \omega_1, \omega_2} \sum_{n_1, n_2=1}^{\infty} \sum_{s's''} [r_s \beta_{s's''}^{qn_1 n_2}(-\omega; \omega_1, \omega_2) + \beta_{s's''}^{\mu n_1 n_2}(-\omega; \omega_1, \omega_2)] [n_1 + n_2] \nabla^{[n_2-1]} \underline{E}(r_{s''}, \omega_2) \nabla^{[n_1-1]} \underline{E}(r_{s'}, \omega_1), \quad (33)$$

$$\underline{p}^{(3)}(\omega) = \frac{1}{6} K_{-\omega, \omega_1, \omega_2, \omega_3} \sum_{n_1, n_2, n_3=1}^{\infty} \sum_{s's''s'''} [r_s \gamma_{s's''s'''}^{qn_1 n_2 n_3}(-\omega; \omega_1, \omega_2, \omega_3) + \gamma_{s's''s'''}^{\mu n_1 n_2 n_3}(-\omega; \omega_1, \omega_2, \omega_3)] [n_1 + n_2 + n_3] \nabla^{[n_3]} \underline{E}(r_{s'''}, \omega_3) \nabla^{[n_2]} \underline{E}(r_{s''}, \omega_2) \nabla^{[n_1]} \underline{E}(r_{s'}, \omega_1), \quad (34)$$

with the new response coefficients related to the previous ones by

$$\alpha_{s's'}^{Mn} = -(-r_{s'})^{[n]} \alpha_{s's'}^{i0} + \alpha_{s's'}^{in}, \quad (35)$$

$$\beta_{s's''}^{Mn_1 n_2} = (-r_{s'})^{[n_1]} (-r_{s''})^{[n_2]} \beta_{s's''}^{i0 n_2} - (-r_{s'})^{[n_1]} \beta_{s's''}^{i0 n_2} - (-r_{s''})^{[n_2]} \beta_{s's''}^{in_1 0} + \beta_{s's''}^{in_1 n_2}, \quad (36)$$

$$\gamma_{s's''s'''}^{Mn_1 n_2 n_3} = -(-r_{s'})^{[n_1]} (-r_{s''})^{[n_2]} (-r_{s'''})^{[n_3]} \gamma_{s's''s'''}^{i000} + (-r_{s'})^{[n_1]} (-r_{s''})^{[n_2]} \gamma_{s's''s'''}^{i00 n_3} + (-r_{s'})^{[n_1]} (-r_{s''})^{[n_2]} \gamma_{s's''s'''}^{i0 n_2 0} + (-r_{s'})^{[n_2]} (-r_{s''})^{[n_3]} \gamma_{s's''s'''}^{in_1 00} - (-r_{s'})^{[n_1]} \gamma_{s's''s'''}^{i0 n_2 n_3} - (-r_{s''})^{[n_2]} \gamma_{s's''s'''}^{in_1 0 n_3} - (-r_{s''})^{[n_3]} \gamma_{s's''s'''}^{in_1 n_2 0} + \gamma_{s's''s'''}^{in_1 n_2 n_3}, \quad (37)$$

where  $i=0$  for  $M=q$  and  $i=1$  for  $M=\mu$  and the frequency dependencies have been dropped for convenience. These equations show the relationship between the response functions with respect to the fields and those with respect to potentials.

For neutral molecules, the distributed (hyper)polarizabilities defined in Eqs. (29)–(31) obey the following sum rules:

$$\sum_s \alpha_{s's'}^{0n} = \sum_{s'} \alpha_{s's'}^{n0} = 0, \quad (38)$$

$$\sum_s \beta_{s's''}^{0n_1 n_2} = \sum_{s'} \beta_{s's''}^{n_1 0 n_2} \dots = 0, \quad (39)$$

$$\sum_s \gamma_{s's''s'''}^{0n_1 n_2 n_3} = \sum_{s'} \gamma_{s's''s'''}^{n_1 0 n_2 n_3} \dots = 0, \quad (40)$$

for all  $n, n_1, n_2, n_3$ . The first equalities follow also from the index interchange symmetries of the distributed (hyper)polarizabilities.

If the applied electric field is uniform over the molecule, all field derivatives vanish and the molecular response can be described by the usual molecular dipole electric polarizability  $\underline{\alpha}$ , first hyperpolarizability  $\underline{\beta}$  and second hyperpolarizability  $\underline{\gamma}$ , which are given in terms of the distributed quantities by

$$\underline{\alpha}(-\omega; \omega) = \sum_{s's'} [r_s \alpha_{s's'}^{q1}(-\omega; \omega) + \alpha_{s's'}^{\mu 1}(-\omega; \omega)], \quad (41)$$

$$\underline{\beta}(-\omega; \omega_1, \omega_2) = \sum_{s's''} [r_s \beta_{s's''}^{q11}(-\omega; \omega_1, \omega_2) + \beta_{s's''}^{\mu 11}(-\omega; \omega_1, \omega_2)], \quad (42)$$

$$\underline{\underline{\gamma}}(-\omega; \omega_1, \omega_2, \omega_3) = \sum_{s's''s'''} [r_s \underline{\underline{\gamma}}_{s's''s'''}^{q111}(-\omega; \omega_1, \omega_2, \omega_3) + \underline{\underline{\gamma}}_{s's''s'''}^{\mu 111}(-\omega; \omega_1, \omega_2, \omega_3)]. \quad (43)$$

These expressions also apply under the assumption that a nonuniform electric field varies only weakly over the dimensions of a molecule. This would be appropriate for a molecule in an electromagnetic field at optical frequencies.

### B. Crystal susceptibilities in terms of distributed (hyper)polarizabilities

Consider a molecular crystal in an external, homogeneous electric field  $\underline{e}$ . In this section we will restrict the multipole expansion to the dipole term, i.e., only the term  $n=n_1=\dots=1$  is retained in Eqs. (26)–(34).

We assume that each molecule can be assigned a volume  $\Omega$  that contains this molecule and no others.<sup>3</sup> The polarization  $\underline{P}(\omega)$ , approximated by the dipole density<sup>13</sup> is given in terms of the distributed moments by

$$\underline{P}(\omega) = v^{-1} \sum_k \underline{p}_k(\omega) = v^{-1} \sum_{ks} [r_{ks} q_{ks}(\omega) + \underline{\mu}_{ks}(\omega)] = v^{-1} \sum_{ks} \underline{U}_{ks}^T \cdot \underline{\Pi}_{ks}(\omega), \quad (44)$$

where  $v$  is the volume of the unit cell, the sum runs over all  $Z$  molecules labeled  $k$  in the unit cell,  $r_{ks}$  is the vector pointing from the molecular origin of molecule  $k$  to the reference point in site  $s$  and  $\underline{p}_k(\omega)$  is the induced dipole moment of molecule  $k$ . This dipole moment is given by Eq. (20), with  $\underline{E}(r, \omega)$  replaced by the respective local field  $\underline{f}(r, \omega)$  effective at  $r$  inside the crystal, caused by the external field  $\underline{e}(\omega)$ .



In turn,  $f(\underline{r}, \omega)$  is given by the sum of the external field  $\underline{e}(\omega)$  and the field created by all the induced moments in the crystal (calculated using multipole lattice sums),<sup>14</sup> except if the point  $\underline{r}$  happens to lie inside the volume  $\Omega$  of a molecule, when the field created by this molecule (the self-field) has to be subtracted. The symbols  $\underline{U}_{ks} = (\underline{r}_{ks}, \underline{1})$  and  $\underline{\Pi}_{ks} = (q_{ks}, \underline{\mu}_{ks})$  have been introduced for convenience.

The quantities  $q_{ks}(\omega), \underline{\mu}_{ks}(\omega)$  in Eq. (44) are the induced charge and dipole in  $\Omega_s$  of molecule  $k$ , and depend in dipole approximation on the local potentials  $\phi_{ks'}^{\text{loc}}$  and the local fields  $\underline{f}_{ks'}$ . The defining equations for  $q_{ks}(\omega), \underline{\mu}_{ks}(\omega)$  follow by comparison of Eqs. (25), (2), and (26)–(28) and can be compactly written in the form

$$\begin{aligned} \underline{\Pi}_{ks} = & \sum_{s'} \underline{\alpha}_{kss'} \cdot \underline{E}_{ks'} + \frac{1}{2} \sum_{s''} \underline{\beta}_{kss''} : \underline{E}_{ks''} \underline{E}_{ks'} \\ & + \frac{1}{6} \sum_{s''s'''} \underline{\gamma}_{kss''s'''} : \underline{E}_{ks''} \underline{E}_{ks'''} \underline{E}_{ks'}, \end{aligned} \quad (45)$$

where the quantity  $\underline{E}_{ks}$  is given by

$$\underline{E}_{ks} = (-\phi_{ks}^{\text{loc}}, \underline{f}_{ks})^T, \quad (46)$$

defined in such a way that the occurring electric fields are positive. According to Eq. (18) the local potential  $\phi_{ks}^{\text{loc}}$  is given in dipole approximation by

$$\phi_{ks}^{\text{loc}} = \phi_{k0}^{\text{loc}} - \underline{r}_{ks} \cdot \underline{f}_{ks}, \quad (47)$$

where  $\phi_{k0}^{\text{loc}}$  is the potential at the molecular origin of molecule  $k$ .

The quantity  $\underline{\alpha}_{kss'}$  in Eq. (45) is given by

$$\underline{\alpha}_{kss'} = \begin{pmatrix} \alpha_{kss'}^{00} & [\alpha_{kss'}^{01}]^T \\ \alpha_{kss'}^{10} & \underline{\alpha}_{kss'}^{11} \end{pmatrix}, \quad (48)$$

and  $\underline{\beta}_{kss''}$  and  $\underline{\gamma}_{kss''s'''}$  are defined similarly. The frequency dependencies have been dropped in Eq. (45).

The induced field quantity  $\underline{F}_{ks}(\omega)$  is given by

$$\underline{F}_{ks}(\omega) = \underline{E}_{ks}^{\text{ext}}(\omega) + (\epsilon_0 v)^{-1} \sum_{k's'} \underline{L}_{kssk's'} \cdot \underline{\Pi}_{k's'}(\omega), \quad (49)$$

where  $\epsilon_0$  is the permittivity of free space and the quantity  $\underline{E}_{ks}^{\text{ext}}(\omega) = (-\phi_{ks}^{\text{ext}}(\omega), \underline{e}(\omega))^T$  is due to the external field  $\underline{e}(\omega)$ , assumed to be homogeneous over the unit cell, where  $\phi_{ks}^{\text{ext}}$  is given by Eq. (47) with loc replaced by ext and  $\underline{f}_{ks}$  by  $\underline{e}$ .  $\underline{L}_{kssk's'}$  is given by

$$\underline{L}_{kssk's'} = \begin{pmatrix} -L_{kssk's'}^{(00)} & [-L_{kssk's'}^{(01)}]^T \\ L_{kssk's'}^{(10)} & \underline{L}_{kssk's'}^{(11)} \end{pmatrix}, \quad (50)$$

with  $L_{kssk's'}^{(00)}$  and  $\underline{L}_{kssk's'}^{(01)}$  being charge–charge and charge–dipole lattice sums,<sup>15</sup> which account for the potential at site  $ks$  due to the charges and dipoles, respectively, of the surrounding molecules, and with  $L_{kssk's'}^{(10)}$  and  $\underline{L}_{kssk's'}^{(11)}$  being Lorentz-factor tensors, which are the dipole–charge lattice sum and the regular part of the dipole–dipole lattice sum, respectively, accounting for the electric field at site  $ks$  due to the surrounding molecules. These quantities are given in Appendix B. Due to their origin from field propagation tensors.

$L_{kssk's'}^{(00)}$  and  $\underline{L}_{kssk's'}^{(11)}$  are symmetric in their indices, while  $\underline{L}_{kssk's'}^{(01)} = -\underline{L}_{k's's'ks}^{(10)}$ . The transpose of the supermatrix  $\underline{L}_{kssk's'}$  is therefore given by

$$\underline{L}_{kssk's'}^T = \underline{L}_{k's's'ks}. \quad (51)$$

Using Eqs. (46), (47), (49)–(51) it can be shown that  $\underline{L}_{kssk's'}$  can be given as

$$\begin{aligned} \underline{L}_{kssk's'} = & \begin{pmatrix} -L_{k0k's'}^{(00)} & [-L_{k0k's'}^{(01)}]^T \\ \underline{0} & \underline{0} \end{pmatrix} \\ & + \begin{pmatrix} \underline{r}_{ks} \cdot \underline{L}_{kssk's'}^{(10)} & \underline{r}_{ks} \cdot \underline{L}_{kssk's'}^{(11)} \\ \underline{L}_{kssk's'}^{(10)} & \underline{L}_{kssk's'}^{(11)} \end{pmatrix}, \end{aligned} \quad (52)$$

$$\begin{aligned} \underline{L}_{k's's'ks}^T = & \begin{pmatrix} -L_{k'0k's'}^{(00)} & [0]^T \\ -\underline{L}_{k'0k's'}^{(01)} & \underline{0} \end{pmatrix} \\ & + \begin{pmatrix} \underline{r}_{k's'} \cdot \underline{L}_{k's's'ks}^{(10)} & [\underline{L}_{k's's'ks}^{(10)}]^T \\ \underline{r}_{k's'} \cdot \underline{L}_{k's's'ks}^{(11)} & \underline{L}_{k's's'ks}^{(11)} \end{pmatrix}, \end{aligned} \quad (53)$$

where  $L_{k0k's'}^{(00)}$  and  $\underline{L}_{k0k's'}^{(01)}$ , etc., account for the potential at the molecular origin of molecule  $k$  due to the surrounding charges and dipoles, respectively.

The terms involving  $\phi_{k0}^{\text{loc}}$  vanish when Eq. (49) is inserted in Eq. (45) owing to the sum rules (38)–(40), and could therefore be discarded, but then the corresponding terms in Eq. (49) have to be identified and subtracted. This could be done using Eq. (52), but the remaining lattice sum tensor, which is the second term on the right-hand side of Eq. (52) does not have the symmetry of the full lattice sum tensor given in Eq. (51), which complicates the treatment. A more convenient way to deal with the  $\phi_{k0}^{\text{loc}}$  terms is to retain them at this point and to show later that they do not contribute to the moments  $\underline{\Pi}_{ks}$ .

In order to express the macroscopic crystal susceptibilities  $\chi_{\parallel}^{(1)}(-\omega; \omega)$ ,  $\chi_{\parallel}^{(2)}(-\omega; \omega_1, \omega_2)$ , and  $\chi_{\parallel}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3)$ , defined by

$$\begin{aligned} \underline{P}(\omega)/\epsilon_0 = & \chi_{\parallel}^{(1)}(-\omega; \omega) \cdot \underline{e}(\omega) \\ & + \chi_{\parallel}^{(2)}(-\omega; \omega_1, \omega_2) : \underline{e}(\omega_2) \underline{e}(\omega_1) \\ & + \chi_{\parallel}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3) : \underline{e}(\omega_3) \underline{e}(\omega_2) \underline{e}(\omega_1) \end{aligned} \quad (54)$$

in terms of the distributed polarizabilities, we adopt a procedure developed by Malagoli and Munn,<sup>16</sup> which allows one to treat the frequency dependence of the susceptibilities in general. According to Eqs. (49) and (45), the local field  $\underline{F}_{ks}$  can be written as

$$\underline{F}_{ks}(\omega) = \underline{F}_{ks}^{(1)}(\omega) + \underline{F}_{ks}^{(2)}(\omega) + \underline{F}_{ks}^{(3)}(\omega), \quad (55)$$

where the  $\underline{F}_{ks}^{(u)}(\omega)$  depend on the external input frequencies  $\omega_i$  as follows:

$$\underline{F}_{ks}^{(1)}(\omega_i) = \underline{E}_{ks}^{\text{ext}}(\omega_i) + (\epsilon_0 v)^{-1} \sum_{k_1s_1} \underline{L}_{kssk_1s_1} \cdot \underline{\Pi}_{k_1s_1}^{(1)}(\omega_i), \quad (56)$$

$$\underline{F}_{ks}^{(2)}(\omega_{i_1} + \omega_{i_2}) = (\epsilon_0 v)^{-1} \sum_{k_1s_1} \underline{L}_{kssk_1s_1} \cdot \underline{\Pi}_{k_1s_1}^{(2)}(\omega_{i_1} + \omega_{i_2}), \quad (57)$$

$$\underline{F}_{ks}^{(3)}(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}) = (\epsilon_0 v)^{-1} \sum_{k_1 s_1} \underline{L}_{k s k_1 s_1} \cdot \underline{\Pi}_{k_1 s_1}^{(3)}(\omega_i + \omega_j + \omega_k). \quad (58)$$

The local field quantities  $\underline{F}^{(2)}$  and  $\underline{F}^{(3)}$  arise from the induced nonlinear moments by way of combined action of two and three input fields, respectively. Taking into account all

the fields present at the molecular site  $k$ , with matching frequency dependence and order of nonlinearity, the induced moments  $\underline{\Pi}_{ks}^{(i)}$  ( $i=1,2,3$ ) are

$$\underline{\Pi}_{ks}^{(1)}(\omega_i) = \sum_{s_1} \underline{\alpha}_{k s s_1}(\omega_i) \cdot \underline{F}_{k s_1}^{(1)}(\omega_i), \quad (59)$$

$$\underline{\Pi}_{ks}^{(2)}(\omega_{i_1} + \omega_{i_2}) = \sum_{s_1} \underline{\alpha}_{k s s_1}(\omega_{i_1} + \omega_{i_2}) \cdot \underline{F}_{k s_1}^{(2)}(\omega_{i_1} + \omega_{i_2}) + 1/2 \sum_{s_1 s_2} \underline{\beta}_{k s s_1 s_2}(-(\omega_{i_1} + \omega_{i_2}); \omega_{i_1}, \omega_{i_2}) : \underline{F}_{k s_2}^{(1)}(\omega_{i_2}) \underline{F}_{k s_1}^{(1)}(\omega_{i_1}), \quad (60)$$

$$\begin{aligned} \underline{\Pi}_{ks}^{(3)}(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}) = & \sum_{s_1} \underline{\alpha}_{k s s_1}(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}) \cdot \underline{F}_{k s_1}^{(3)}(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}) + 1/2 \hat{I}_{\omega_{i_1}, \omega_{i_2}, \omega_{i_3}} \\ & \times \sum_{s_1 s_2} \underline{\beta}_{k s s_1 s_2}(-(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}); \omega_{i_1}, \omega_{i_2} + \omega_{i_3}) : \underline{F}_{k s_2}^{(2)}(\omega_{i_2} + \omega_{i_3}) \underline{F}_{k s_1}^{(1)}(\omega_{i_1}) \\ & + 1/6 \sum_{s_1 s_2 s_3} \underline{\gamma}_{k s s_1 s_2 s_3}(-(\omega_{i_1} + \omega_{i_2} + \omega_{i_3}); \omega_{i_1}, \omega_{i_2}, \omega_{i_3}) : \underline{F}_{k s_3}^{(1)}(\omega_{i_3}) \underline{F}_{k s_2}^{(1)}(\omega_{i_2}) \underline{F}_{k s_1}^{(1)}(\omega_{i_1}), \end{aligned} \quad (61)$$

where  $\hat{I}_{\omega_{i_1}, \omega_{i_2}, \omega_{i_3}}$  generates additional terms by interchanging the frequencies  $\omega_{i_1}, \omega_{i_2}, \omega_{i_3}$  together with their associated indices.

The coupled set of Eqs. (56)–(61) can be successively solved to yield the  $\underline{\Pi}_{ks}^{(i)}$  as functions of the macroscopic field quantities  $\underline{E}_{ks}^{\text{ext}}(\omega)$ . Equation (56) with (59) gives

$$\underline{F}_{ks}^{(1)}(\omega_i) = \sum_{k_1 s_1} \underline{D}_{k s, k_1 s_1}(\omega_i) \cdot \underline{E}_{k_1 s_1}^{\text{ext}}(\omega_i), \quad (62)$$

where the quadratic supermatrix  $\underline{D}$  of dimension  $4Zn_s$  is the inverse of another supermatrix  $\underline{X}$  built up from  $4 \times 4$  matrices

$$\underline{X}_{k_1 s_1, k' s'} = \delta_{k_1 k'} \delta_{s_1 s'} \underline{I} - (\epsilon_0 v)^{-1} \sum_{s_2} \underline{L}_{k_1 s_1 k' s_2} \cdot \underline{\alpha}_{k' s_2 s'}. \quad (63)$$

If Eq. (53) is inserted into this equation, the terms involving the lattice sums at the molecular origin disappear because of the sum rule Eq. (38). Therefore only the Lorentz-factor tensors  $\underline{L}^{(10)}$  and  $\underline{L}^{(11)}$  need to be calculated for  $\underline{D}$ .

On substitution of Eq. (62) in (59),  $\underline{\Pi}_{ks}^{(1)}$  follows in terms of  $\underline{E}_{ks}^{\text{ext}}$ . Inserting Eqs. (57) and (62) into Eq. (60) yields an equation that can be solved to give  $\underline{\Pi}_{ks}^{(2)}$  in terms of  $\underline{E}_{ks}$ . Similarly, Eq. (61) can be solved with  $\underline{\Pi}_{ks}^{(2)}$  in Eq. (57) and Eq. (62) to give  $\underline{\Pi}_{ks}^{(3)}$  as a function of  $\underline{E}_{ks}$ . The macroscopic susceptibilities  $\chi_{ks}^{(1)}$ ,  $\chi_{ks}^{(2)}$ , and  $\chi_{ks}^{(3)}$  can then be obtained by inserting the  $\underline{\Pi}_{ks}^{(i)}$  into Eq. (44) and comparing with Eq. (54). At this point it is necessary to show that the terms involving  $\phi_{k0}^{\text{ext}}$  in the expressions for the  $\underline{\Pi}_{ks}^{(i)}$  vanish. We will show this explicitly for  $\underline{\Pi}_{ks}^{(1)}$ , which is given by

$$\begin{aligned} \underline{\Pi}_{ks}^{(1)} = & \sum_{s' k_1 s_1} \underline{\alpha}_{k s s'} \cdot \underline{D}_{k s', k_1 s_1} \\ & \cdot [(-\phi_{k_1 0}^{\text{ext}}, 0, 0, 0)^T + \underline{U}_{k_1 s_1} \cdot \underline{e}], \end{aligned} \quad (64)$$

where we have separated the terms involving  $\phi_{k_1 0}^{\text{ext}}$  and  $\underline{e}$  in  $\underline{E}_{ks}$ . In order to show that the first term vanishes, we use the following identity:

$$\underline{D}_{k s', k_1 s_1} = \sum_{k_2 s_2 s_3} \underline{L}_{k s' k_2 s_2} \cdot \underline{D}_{k_2 s_2 k_1 s_3} \cdot \underline{\alpha}_{k_1 s_3 s_1} + \underline{I} \delta_{k k_1} \delta_{s' s_1}, \quad (65)$$

which is a generalization of a relationship used previously<sup>17</sup> for the connection of susceptibilities with molecular (hyper)polarizabilities in the point dipole approximation. Inserting this expression into Eq. (64), we see with Eq. (48) that the first term in Eq. (64) is zero due to the sum rule Eq. (38). Similar arguments hold in the case of  $\underline{\Pi}_{ks}^{(2)}$  and  $\underline{\Pi}_{ks}^{(3)}$ , except that here the sum rules Eq. (39) and (40) are involved, too.

The final results for the susceptibilities are

$$\chi_{ks}^{(1)}(\omega) = (\epsilon_0 v)^{-1} \sum_{k s s'} \underline{U}_{k s} \cdot \underline{\alpha}_{k s s'}(\omega) \cdot \underline{d}_{k s'}(\omega), \quad (66)$$

$$\begin{aligned} \chi_{ks}^{(2)}(\omega) = & (2\epsilon_0 v)^{-1} \sum_{k s s' s''} \underline{d}_{k s'}(\omega)^T \\ & \cdot \underline{\beta}_{k s s' s''}(-\omega; \omega_2, \omega_1) : [{}_{1,3} \underline{d}_{k s'}(\omega_1) \underline{d}_{k s''}(\omega_2)], \end{aligned} \quad (67)$$

$$\chi_{ks}^{(3)}(\omega) = \chi_{ks}^{(3)\text{direct}}(\omega) + \chi_{ks}^{(3)\text{cascading}}(\omega), \quad (68)$$

$$\begin{aligned} \underline{\chi}_{\text{direct}}^{(3)}(\omega) &= (6\epsilon_0 V)^{-1} \sum_{k s s' s'' s'''} \underline{d}_{k s}(\omega)^T \\ &\cdot \underline{\gamma}_{k s s'' s'' s'}(-\omega; \omega_3, \omega_2, \omega_1) \\ &\cdot :_{[1,3,5]}[\underline{d}_{k s'}(\omega_1) \underline{d}_{k s''}(\omega_2) \underline{d}_{k s'''}(\omega_3)], \end{aligned} \quad (69)$$

$$\begin{aligned} \underline{\chi}_{\text{cascading}}^{(3)}(\omega) &= \frac{1}{4(\epsilon_0 V)^2} \hat{I}_{\omega_1, \omega_2, \omega_3} \sum_{k s} \underline{d}_{k s}(\omega)^T \\ &\cdot \sum_{k' s' s'' s'''} \left[ \sum_{k_2 s_2 s_3 s_4} \underline{\beta}_{k s s' s_2}(-\omega; \omega_3, \omega_1 + \omega_2) \right. \\ &\cdot \underline{L}_{k s_2, k_2 s_3} \cdot \underline{D}_{k_2 s_3 k' s_4}(\omega_1 + \omega_2) \\ &\cdot \left. \underline{\beta}_{k' s_4 s'' s'''}(-(\omega_1 + \omega_2); \omega_2, \omega_1) \right] \\ &\cdot :_{[1,3,5]}[\underline{d}_{k' s'''}(\omega_1) \underline{d}_{k' s''}(\omega_2) \underline{d}_{k s'}(\omega_3)], \end{aligned} \quad (70)$$

where  $:_{[1,3]}$  denotes a nonstandard double contraction with the first and third index of the tensor which follows, and  $:_{[1,3,5]}$  likewise a triple contraction. Here the local field tensor  $\underline{d}_{k s}$  is defined by

$$\underline{d}_{k s} = \sum_{k_1 s_1} \underline{D}_{k s k_1 s_1} \cdot \underline{U}_{k_1 s_1}. \quad (71)$$

The equations may be compared with those resulting in the theory of the submolecule treatment, which was developed by Hurst and Munn<sup>18</sup> to take into account effects on the crystal susceptibilities arising from the finite sizes and shapes of the molecules composing the crystal. In this theory the molecules are divided into submolecules, assuming that every submolecule gives the same contribution to the susceptibilities. The effect of the crystal environment is again calculated using the rigorous local field approach. The submolecules are in general chosen in such a way as to describe approximately the expected distribution of the polarizability over the molecule, but the choice is rather arbitrary. In spite of this arbitrariness the treatment has been shown to predict qualitatively correct crystal susceptibilities.<sup>16</sup> For small and compact molecules such as urea and benzene the theory predicts  $\underline{\chi}_{\text{c}}^{(1)}$  even quantitatively.<sup>19,20</sup> The main difference between the theory presented here and the submolecule treatment consists in a more realistic description of the charge distribution of the molecules in the crystalline environment. It can be shown by neglecting the charge terms that the Eqs. (66)–(67) reduce to those of the submolecule treatment [see, e.g., Eqs. (39)–(40) in Ref. 14 and Eqs. (4) and (6) in Ref. 16].

In the case of distributed polarizabilities, different partition schemes have been used,<sup>2,21,22</sup> but apparently the most stable one in terms of basis set dependence and physically plausible contributions has been found to be that based on the theory of atoms in molecules, developed by Bader and co-workers.<sup>23,24</sup> In this theory, three-dimensional space is partitioned into regions  $\Omega_s$  (basins) bounded by surfaces  $S_s(\underline{r})$  on which the electronic charge density  $\rho(\underline{r})$  satisfies the zero-flux condition  $\nabla \rho(\underline{r}) \cdot \underline{n}(\underline{r}) = 0 \forall \underline{r} \in S_s(\underline{r})$ . We shall apply this distribution scheme here to the unperturbed mol-

ecule. For a molecule in an external electric field in the formulation by Cioslowski<sup>25</sup> the atoms in molecules approach requires the consistent application of the zero-flux condition on the *perturbed* molecule, incorporating surface relaxation effects due to the electric field. Such an approach, however, does not lead to a real-space partitioning of the molecular response functions as in Eqs. (26)–(28) or (32)–(34).<sup>26</sup> Our objective is a realistic description of the spatial distribution of the charge density response rather than a rigorous atomic partition of the (hyper)polarizabilities, which would be able to reproduce atomic multipole moments at any finite external field, including the effect of the shift of the interatomic boundaries. Further, both approaches conserve the total (hyper)polarizabilities and the invariance with respect to interchange of the perturbation operators.<sup>25,26</sup> Therefore, we consider the application of the above distribution scheme on the unperturbed molecule sufficient for our purposes.

### III. APPLICATION TO UREA

As an illustrative example, we have chosen to calculate the linear and quadratic susceptibilities of the urea crystal, using the static distributed polarizabilities and first hyperpolarizabilities calculated at the SCF level. Urea is a standard NLO crystal that we have studied previously,<sup>20</sup> so that direct comparisons can be made.

The atomic multipole integrals required for the calculation of the distributed (hyper)polarizabilities were provided by a modified version of the PROAIM program<sup>27</sup> (as described in Ref. 30). The distributed static polarizabilities and first hyperpolarizabilities were determined at the SCF level of theory using the program FOURIER.<sup>28</sup>

The polarization-consistent Sadlej basis set has been used for the calculation of the molecular properties. The molecular geometry (at 123 K) has been taken from Ref. 29, where the crystal structure of urea at 12, 60, and 123 K was determined by neutron diffraction. The molecular  $z$ -axis points from the carbon to the oxygen atom, the  $y$ -axis lies in the molecular plane, and the  $x$ -axis completes the orthogonal right-handed Cartesian system. The origin is placed at the molecular center of mass.

Owing to the limited precision of the numerical integration procedure, the reconstructed hyperpolarizabilities calculated by Eq. (42) differ slightly from the molecular hyperpolarizabilities obtained by a coupled perturbed Hartree–Fock (CPHF) calculation applying a homogeneous electric field to the molecule, as can be seen from the last two lines in Tables I and II, where both quantities are given. For the polarizability  $\alpha$ , the differences are lower than 1% and for  $\beta$ , lower than 3%. These inaccuracies may also mean that the molecular charge is not fully conserved. An *ad hoc* correction scheme as already used in Ref. 30, has been employed to remedy this deficiency.

In Table I we present the unique components of the distributed polarizabilities  $\alpha_{s s'}^{00}$ ,  $\alpha_{s s'}^{01}$ , and  $\alpha_{s s'}^{11}$ , of urea with an absolute value larger than 0.1 a.u. and in Table II the unique components of the distributed first hyperpolarizabilities that are larger than certain given thresholds. (The complete set of



TABLE I. Unique components of the distributed polarizabilities of urea larger than 0.1 a.u., reconstructed polarizabilities  $\alpha_{ss'}^{\text{rec}}$  and molecular polarizabilities calculated by CPHF,  $\alpha_{ij}^{\text{CPHF}}$ , all units in a.u., conversion factors to other units:  $\alpha^{00}$ : 1 a.u.=51.918 $\times 10^{-10}$  esu=0.588 76 $\times 10^{-20}$  C<sup>2</sup> J<sup>-1</sup>;  $\alpha^{10}$ ,  $\alpha^{01}$ : 1 a.u.=2.8003 $\times 10^{-17}$  esu=0.311 56 $\times 10^{-30}$  m C<sup>2</sup> J<sup>-1</sup>;  $\alpha^{11}$ : 1 a.u.=0.148 185 $\times 10^{-24}$  esu=0.164 87 $\times 10^{-40}$  (C m)<sup>2</sup> J<sup>-1</sup>.

$ss'$	$\alpha_{ss'}^{00}$	$\alpha_{ss',j}^{01}$		$\alpha_{i,ss'}^{10}$ <sup>a</sup>	$\alpha_{ij,ss'}^{11}$			
		$i=y$	$z$	$i=z$	$ij=xx$	$yy$	$zy$	$zz$
C C	0.91				0.860	0.238		0.209
C O	-0.384		-0.129		0.223			-0.157
C N1	-0.241							
O O	1.034		0.536			5.638		3.918
O N1	-0.211		-0.127	-0.106	-0.263		-0.138	
N1 N1	1.406	0.301	-0.195		7.710	3.280	-0.140	3.054
N1 N2	-0.124				-0.244			
N1 H11	-0.375	-0.193	-0.104		0.164			0.109
N1 H12	-0.403		0.241		0.190	0.169		
H11 H11	0.545	0.298	0.152		0.240	0.351		0.242
H12 H12	0.583		-0.369		0.290	0.258		0.424
$\alpha_{ij}^{\text{rec}}$					24.424	35.883	0.000	37.210
$\alpha_{ij}^{\text{CPHF}}$					24.451	35.910	0.000	37.269

<sup>a</sup>Only components given that are not equal by symmetry to any of the  $\alpha_{ss',i}^{01}$  shown.

TABLE II. Unique components of the distributed first hyperpolarizabilities of urea with absolute values larger than 0.3 a.u. ( $\beta_{ss's''}^{000}$ ,  $\beta_{ss's'',i}^{001}$ ), 0.5 a.u. ( $\beta_{ss's'',ij}^{011}$ ,  $\beta_{ij,ss's''}^{110}$ ), and 1 a.u. ( $\beta_{ijk,ss's''}^{111}$ ); reconstructed first hyperpolarizabilities  $\beta_{ijk}^{\text{rec}}$  and molecular first hyperpolarizabilities calculated by CPHF,  $\beta_{ijk}^{\text{CPHF}}$ , all units in a.u., conversion factors to other units:  $\beta^{000}$ : 1 a.u.=5.8306 $\times 10^{-13}$  esu=2.1639 $\times 10^{-22}$  C<sup>3</sup> J<sup>-2</sup>;  $\beta^{001}$ ,  $\beta^{010}$ ,  $\beta^{100}$ : 1 a.u.=3.0854 $\times 10^{-16}$  esu=1.1451 $\times 10^{-32}$  C<sup>3</sup> m J<sup>-2</sup>;  $\beta^{011}$ ,  $\beta^{101}$ ,  $\beta^{110}$ : 1 a.u.=1.6327 $\times 10^{-24}$  esu=6.0596 $\times 10^{-43}$  C<sup>3</sup> m<sup>2</sup> J<sup>-2</sup>;  $\beta^{111}$ : 1 a.u.=0.864 $\times 10^{-32}$  esu=0.320 66 $\times 10^{-52}$  C<sup>3</sup> m<sup>3</sup> J<sup>-2</sup>.

$ss's''$	$\beta_{ss's''}^{000}$	$\beta_{ss's'',i}^{001}$		$\beta_{ss's'',ij}^{011}$			$\beta_{ij,ss's''}^{110}$ <sup>a</sup>	
		$i=y$	$z$	$ij=xx$	$yy$	$zz$	$xx$	$yy$
C C C	-0.44			-0.57				
C C O	-0.93							
C O O				0.90	0.95			
C C N1	-0.39							
O O O	1.64			-4.66	-3.64		-2.55	
O O N1							0.98	0.82
O N1 N1				2.45	0.72			
N1 N1 N1	1.00			-7.91	-1.55	-1.06		
N1 N2 N2				0.78				
N1 N1 H11							1.79	
N1 N1 H21							1.85	0.51
N1 H11 H11	0.49	0.46			0.66			
N1 H12 H12	0.49		-0.55			0.87		
H11 H11 H11	-0.69	-0.69	-0.34	-0.50	-1.09	-0.56		
H12 H12 H12	-0.71		0.86	-0.62	-0.52	-1.41		
	$\beta_{ij,ss's''}^{110}$ <sup>a</sup>	$\beta_{ijk,ss's''}^{111}$						
$ss's''$	$zz$	$ijk=xyx$	$xxz$	$zxx$	$yyy$	$yyz$	$yzz$	$zzz$
O O O			-11.50	-11.50		-14.01		-18.30
O O N1	0.61	1.07	-1.54			-1.30		
O N1 N1			2.29					
N1 N1 N1		-12.61	8.66	8.66	-7.72	3.32	-2.52	2.56
N1 N1 N2		-1.98						
N1 N1 H12				1.24				
H11 H11 H11					-2.05			
H12 H12 H12								2.70
$\beta_{ijk}^{\text{rec}}$		0.0	16.3	16.3	0.0	-44.1	0.0	67.9
$\beta_{ijk}^{\text{CPHF}}$		0.0	16.8	16.8	0.0	-44.6	0.0	68.5

<sup>a</sup>Only components given that are not equal by symmetry to any of the  $\beta_{ss's'',ij}^{011}$  shown.

TABLE III. Calculated and experimental components of the linear ( $\chi^{(1)}$ ) and quadratic ( $\chi^{(2)}/10^{-12}$  V<sup>-1</sup> m) macroscopic susceptibility tensors of the urea crystal.

	$\chi_{aa}^{(1)}$	$\chi_{cc}^{(1)}$	$\chi_{abc}^{(2)}$
Distributed	1.085	1.414	-1.07
4 Submolecules	1.009	1.443	-1.98
Point dipole	1.038	1.353	-1.97
Expt.	1.221 <sup>a</sup>	1.569 <sup>a</sup>	2.8 <sup>a,b</sup>

<sup>a</sup>At  $\lambda = 597$  nm.

<sup>b</sup>Second harmonic generation (Ref. 31). Only the absolute value was determined.

data is available from the authors.) The data show that the most polarizable centers are the oxygen and the nitrogen atoms, while the carbon atom has low polarizabilities and first hyperpolarizabilities, due to the three electron-withdrawing atoms attached to it (the atomic charge on C is 2.27 |e|).

Using Eqs. (66) and (67), the macroscopic susceptibilities  $\chi^{(1)}$  and  $\chi^{(2)}$  can be calculated from the distributed (hyper)polarizabilities. The results are shown in Table III, together with experimental results and results obtained using the point dipole approximation and the submolecule treatment of Hurst and Munn, using one submolecule on each C, O, and N atom. In order to be comparable, the reconstructed molecular (hyper)polarizabilities were used in the latter two calculations. The data show that the values of the calculated linear susceptibility for the different calculational methods are quite similar, while the quadratic susceptibility calculated with the distributed model is only about half the value calculated with the other methods. We cannot expect the calculated susceptibilities to reproduce the experimental data exactly, as neither electronic correlation nor dispersion effects are included in the molecular properties. Further, our results are calculated for a urea crystal at  $T = 123$  K, while the experiments were performed at room temperature. It has been shown in Ref. 20 that, using the same basis set, both the point dipole approximation and the 4 submolecule model are able to reproduce approximately the experimental values for the first order susceptibilities  $\chi_{ii}^{(1)}$ , if electronic correlation at the MP2 level, frequency dispersion and the effect of the permanent crystal field are taken into account. Further, the inclusion of those effects increased the absolute value of the quadratic susceptibility  $\chi_{abc}^{(2)}$  by a factor of about 2.6, yielding values (4.7 pm/V and 4.8 pm/V) that are much too large compared with the experimental data. Applying this enhancement factor to the value calculated here with the distributed model gives exactly the experimental value, 2.8 pm/V. Although this agreement is certainly fortuitous, it nevertheless shows that the value for  $\chi_{abc}^{(2)}$  in the distributed model would probably be much closer to the experimental value, if the additional effects mentioned are included, than those calculated with the simpler point dipole and submolecule models.

Using  $E_{ks}^{\text{ext}} = 0$  in Eq. (49) and adding the permanent distributed charges and dipoles  $\Pi_{ks}^{(0)}$  to the induced ones in Eq. (45) allows us to calculate the permanent electric local field  $f_{ks}^{(0)}$  at the different sites in the molecule, after subtracting the potential at the molecular origin. In a first approximation, the

TABLE IV. Permanent local electric field at the atoms of an urea molecule in the crystal, due to the charges ( $F_s^{(q0)}$ ), the dipoles ( $F_s^{(\mu0)}$ ) and due to both moments ( $F_s^{(0)} = F_s^{(q0)} + F_s^{(\mu0)}$ ) of the surrounding molecules; due to the crystal symmetry the  $x$ -components are zero. All values are in GV m<sup>-1</sup>.

$s$	$F_{y,s}^{(q0)}$	$F_{z,s}^{(q0)}$	$F_{y,s}^{(\mu0)}$	$F_{z,s}^{(\mu0)}$	$F_{y,s}^{(0)}$	$F_{z,s}^{(0)}$
C	0.00	-22.52	0.00	7.52	0.00	-14.99
O	0.00	-24.53	0.00	7.21	0.00	-17.32
N1	2.89	-16.43	0.49	5.94	3.35	-10.48
H11	23.07	-11.34	-3.38	5.25	19.69	-6.10
H12	-16.18	-22.92	6.58	6.47	-9.60	-16.45
N2	-2.89	-16.43	-0.49	5.94	-3.35	-10.48
H21	-23.07	-11.34	3.38	5.25	-19.69	-6.10
H22	16.18	-22.92	-6.58	6.47	9.60	-16.45

contribution of the distributed hyperpolarizabilities may be ignored, whence the field  $f_{ks}^{(0)}$  is given by

$$\underline{U}_{ks}^T \cdot \underline{f}_{ks}^{(0)} = (\epsilon_0 V)^{-1} \sum_{k_1 s_1 k_2 s_2} \underline{D}_{ks, k_1 s_1}^f \cdot \underline{L}_{k_1 s_1, k_2 s_2}^f \cdot \underline{\Pi}_{k_2 s_2}^{(0)}, \quad (72)$$

where  $\underline{L}_{k_1 s_1, k_2 s_2}^f$  denotes the second term on the right-hand side of Eq. (52) and  $\underline{D}^f$  is the inverse tensor of the  $\underline{X}$  tensor given in Eq. (63) with  $\underline{L}$  replaced by  $\underline{L}^f$ . The left-hand side of Eq. (72) is the four component vector  $(\underline{L}_{ks} \cdot \underline{f}_{ks}^{(0)}, \underline{f}_{ks}^{(0)})^T$ .

The fields calculated within this approximation are given in Table IV. It is evident that the permanent local field is strongly inhomogeneous, even over this comparatively small molecule, indicating that a distributed description would be mandatory in a further refinement of the susceptibility calculations, where the permanent local field effect on the (hyper)polarizabilities would have to be considered.<sup>20</sup>

Also given in Table IV are the contributions to the total permanent local field caused by the distributed charges and dipoles alone (i.e., the fields produced by the two permanent contributions  $q_{ks}^{(0)}$  and  $\mu_{ks}^{(0)}$  occurring in  $\underline{\Pi}_{ks}^{(0)}$ , including the fields due to the *induced* charges and dipoles). The data show that the most important contribution to the total field comes from the charges and that the dipole fields nearly always oppose the charge fields. If the fields from higher distributed multipoles follow the same opposing behavior, their contributions could change the local field considerably. In order to have a reliable description of the permanent local field, the contributions from distributed multipoles higher than dipole (and from the hyperpolarizabilities) should therefore be included.

## IV. CONCLUSIONS

We have extended Stone's treatment of the nonlocal polarizability function to nonlocal first and second dipolar hyperpolarizability functions, introducing the respective distributed hyperpolarizabilities by way of multicentered multipole expansions. Extensions to higher multipolar electric hyperpolarizabilities and magnetic hyperpolarizabilities can easily be carried out. The response functions have been expressed both in terms of charge density changes related to changes in the electric potential, which is suitable for problems involving the calculation of intermolecular interaction energies, and in terms of dipole density changes related to

changes of the electric field, which is the more customary point of view in the field of nonlinear optics. With the help of the distributed (hyper)polarizabilities a theory for the macroscopic nonlinear optical susceptibilities of molecular crystals has been developed, which is formally similar to existing theories that go beyond the point dipole approximation, but provides a more satisfactory distribution scheme for the molecular response, if coupled with a rigorous partitioning scheme like Bader's atoms in molecules approach.

The application of the formalism to the macroscopic susceptibilities of the urea crystal shows that even for this quite small molecule the multicentred description of the molecular response yields very different results for the quadratic susceptibility, compared to the point-dipole approximation, and will probably be in much better agreement with experimental data once correlation effects, dispersion and permanent field effects are taken into account. For larger molecules the incapability of the monocentred description to describe the anisotropy of the charge density will become much more pronounced and it will be necessary to use more distributed schemes. These might use the rigorous method presented here, perhaps simplified by integrating over basins that represent functional groups rather than individual atoms, or else simpler schemes, developed previously, that distribute the response functions in more intuitive ways. But the results of the present work on urea show that the effects of the strongly inhomogeneous permanent local field can be described more accurately only by methods using physically meaningful distribution schemes.

## APPENDIX A

Here we show that  $\phi(r_s)$  can be given by Eq. (18). Expanding the potential  $\phi(r)$  around  $r_0=(0,0,0)$ , we can write

$$\phi(r) - \phi(r_0) = - \sum_{n=1}^{\infty} \frac{1}{n!} r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0). \quad (\text{A1})$$

We want to show that

$$\begin{aligned} & - \sum_{n=1}^{\infty} \frac{1}{n!} r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0) \\ &= \sum_{n=1}^{\infty} \frac{1}{n!} [-r_s]^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_s). \end{aligned} \quad (\text{A2})$$

The terms  $\nabla^{[n-1]} \underline{E}(r_s)$  can be expressed as series around the origin, by means of Eq. (A1):

$$\begin{aligned} & \nabla^{[n-1]} \underline{E}(r_s) \\ &= \sum_{m=n}^{\infty} \frac{1}{(m-n)!} r_s^{[m-n]} [m-n] \nabla^{[m-1]} \underline{E}(r_0). \end{aligned} \quad (\text{A3})$$

Inserting into Eq. (A2) gives

$$\begin{aligned} & - \sum_{n=1}^{\infty} \frac{1}{n!} r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0) \\ &= \sum_{m=1}^{\infty} \sum_{n=m}^{\infty} \frac{1}{m!(n-m)!} (-1)^m r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0). \end{aligned} \quad (\text{A4})$$

Comparing terms of equal order  $n-1$  of derivatives yields

$$\begin{aligned} & - \frac{1}{n!} r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0) \\ &= \sum_{m=1}^n \frac{1}{m!(n-m)!} (-1)^m r_s^{[n]} [n] \nabla^{[n-1]} \underline{E}(r_0) \\ &\Rightarrow - \frac{1}{n!} = \sum_{m=1}^n \frac{(-1)^m}{m!(n-m)!}. \end{aligned} \quad (\text{A5})$$

The last equation can be recast into

$$\sum_{m=0}^n \binom{m}{n} (-1)^{m+1} = 0, \quad (\text{A6})$$

which is a known property of the binomial coefficients.

## APPENDIX B

The equations for the calculation of a general Lorentz-factor tensor (that is, a dipole–multipole lattice sum) in the point-dipole approximation have been given in Ref. 32. The extension for the dipole–charge and dipole–dipole tensors to the case of a molecule composed of several subunits has been treated by Bounds and Munn<sup>33</sup> for the calculation of the effects of a localized charge on the polarization energy of a crystal. The charge–charge lattice sum  $L_{k'sk's'}^{(00)}$  is the essential ingredient of the Madelung constant and the charge–dipole lattice sum  $L_{ks,k's'i}^{(01)}$  is determined by  $L_{ks,k's'i}^{(01)} = -L_{k's'i,ks}^{(10)}$ . It is shown in connection with Eq. (63) that  $L_{k'sk's'}^{(00)}$  is not needed for the calculation of the susceptibilities and will therefore not be given here.

The Lorentz-factor tensors  $L_{k'si,k's'i}^{(10)}$ , and  $L_{k'si,k's'i}^{(11)}$  in Eq. (50) for the reference unit cell  $l=0$  (in component form) are

$$\begin{aligned} L_{k'si,k's'i}^{(10)} = & - \frac{v_a R^2}{4\pi} \left( \delta_{kk'} (1 - \delta_{s's'}) H_i^{q,0} [R | r_{0k's'} - r_{0ks} |] \right. \\ & \left. + \sum_l (1 - \delta_{l0} \delta_{kk'}) H_i^{q,1} [R | r_{lk's'} - r_{lks} |] \right) \\ & + \frac{\pi}{2R^2} \sum_{h \neq 0} G[(\pi^2/R^2) \underline{y}(h)^2] y_i(h) \\ & \times \sin[2\pi \underline{y}(h) \cdot (r_{0ks} - r_{0k's'})], \end{aligned} \quad (\text{B1})$$

$$\begin{aligned}
L_{k'si,k's'j}^{(11)} &= \frac{v_a R^3}{3\pi^{3/2}} \delta_{ij} \delta_{s's'} \delta_{kk'} + \frac{v_a R^3}{4\pi} \\
&\times \left\{ \delta_{kk'} (1 - \delta_{s's'}) H_{ij}^{\mu,0} [R|r_{0ks'} - r_{0ks}|] \right. \\
&+ \sum_l (1 - \delta_{l0} \delta_{kk'}) H_{ij}^{\mu,1} [R|r_{lk's'} - r_{0ks}|] \left. \right\} \\
&- \frac{\pi^2}{R^2} \sum_{h \neq 0} y_i(h) y_j(h) G[(\pi^2/R^2) \underline{y}(h)^2] \\
&\times \cos[2\pi \underline{y}(h) \cdot (r_{0ks} - r_{0k's'})], \quad (\text{B2})
\end{aligned}$$

where

$$\begin{aligned}
H_i^{q,n} [|\underline{x}|] &= \frac{x_i}{|\underline{x}|^3} \left[ -\delta_{n0} \operatorname{erf}(|\underline{x}|) + \delta_{n1} \operatorname{erfc}(|\underline{x}|) \right. \\
&+ \left. \frac{2|\underline{x}|}{\pi^{1/2}} \exp\{-|\underline{x}|^2\} \right], \quad (\text{B3})
\end{aligned}$$

$$\begin{aligned}
H_{ij}^{\mu,n} [|\underline{x}|] &= \frac{1}{|\underline{x}|^3} \left[ -\delta_{ij} + \frac{3x_i x_j}{|\underline{x}|^2} \right] \left[ -\delta_{n0} \operatorname{erf}(|\underline{x}|) \right. \\
&+ \left. \delta_{n1} \operatorname{erfc}(|\underline{x}|) \right] + \frac{1}{|\underline{x}|^2} \left[ -\delta_{ij} + \frac{3x_i x_j}{|\underline{x}|^2} + 2x_i x_j \right] \\
&\times \frac{2}{\pi^{1/2}} \exp\{-|\underline{x}|^2\}, \quad (\text{B4})
\end{aligned}$$

$$G(x) = \frac{1}{x} \exp(-x). \quad (\text{B5})$$

Here  $v_a$  is the volume of the unit cell,  $\underline{y}(l)$  are reciprocal lattice vectors,  $\operatorname{erf}(x) = 2/\pi^{1/2} \int_0^x \exp(-x^2)$  is the error function,  $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$  is the complementary error function and  $R$  is a parameter that determines the rate of convergence of the lattice sums: usually<sup>32</sup> it is sufficient to set  $R = \pi^{1/2} v_a^{-1/3}$ .

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