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Non-Linear Optical constants from molecular hyperpolarisabilities: I. Iterative solution of quadratic tensor equations for mutual polarisation

Wynand S. Verwoerd

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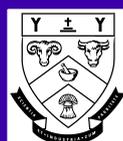
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The Editor
Applied Computing, Mathematics and Statistics Group
Applied Management and Computing Division
PO Box 84
Lincoln University
Canterbury
NEW ZEALAND

Email: computing@lincoln.ac.nz

Non-linear optical constants from molecular hyperpolarisabilities: I. Iterative solution of quadratic tensor equations for mutual polarisation.

Wynand. S. Verwoerd, Centre for Advanced Computational Solutions, AMAC
Division, P.O. Box 84, Lincoln University, Canterbury, NEW ZEALAND

Email: verwoerw@tui.lincoln.ac.nz

ABSTRACT

To describe mutual polarisation in bulk materials containing high polarisability molecules, local fields beyond the linear approximation needs to be included. A second order tensor equation is formulated that describes this in the case of crystalline or at least locally ordered materials such as an idealised polymer. It is shown that this equation is solved by a set of recursion equations that relate the induced dipole moment, linear polarisability and first hyperpolarisability in the material to the intrinsic values of the same properties of isolated molecules. From these, macroscopic susceptibility tensors up to 2nd order can be calculated for the material.

1. Introduction.

In developing polymer materials with the required optical properties needed for non-linear optics technology, great advances have been made in recent years to design chromophore molecules with enhanced polarisabilities. For example, a highly successful strategy was developed by Marder et al ⁽¹⁾⁻⁽³⁾ based on a donor-acceptor mechanism. By carefully matching the donor and acceptor strengths and the energetics of charge transfer, e.g. by selecting acceptor structures that can compensate for the loss of aromaticity on polarisation in the intervening conductor part of the molecule, the hyperpolarisability of chromophores has been enhanced by orders of magnitude. For example, the simple prototype donor-acceptor molecule p-nitroaniline has a first hyperpolarisability ⁽⁴⁾ $\beta=6.3 \times 10^{-50}$ SI units at $\omega=1.17$ eV, compared to the values⁽⁵⁾ of 0.8×10^{-50} and 0.4×10^{-50} respectively of its non-push-pull precursor molecules nitrobenzene and aniline. Moreover, fine-tuning of the kind referred to has led to the production of several molecules with β values^{(2),(3)} in a range as high as 400×10^{-50} to 800×10^{-50} SI units.

In view of these very high hyperpolarisabilities, it is appropriate to re-examine the approximations that are customarily used to calculate linear and non-linear bulk susceptibilities from the corresponding molecular polarisabilities. This problem has a long history, having been studied by Lorentz ⁽⁶⁾ and a local field application to non-linear optical properties introduced by Armstrong et al ⁽⁷⁾ is commonly used and is, for example, reviewed in the textbook by Butcher and Cotter ⁽⁸⁾. A key assumption in this treatment is that the local field experienced by a molecule is mainly due to the linear polarisability of surrounding molecules. As a result, the equation for the local field is

effectively linearised and can be readily solved. However, with increasing non-linear polarisabilities this approximation must break down and it is of interest to solve the full non-linear equation.

Another notable property of donor-acceptor molecules, is that their polarisabilities are highly anisotropic tensors. This is a direct result of the underlying mechanism, since the donor and acceptor groups are spatially localised and it is mainly charge transfers along the geometrical axis that connects them, that is enhanced. This observation calls into question the adequacy of describing such molecules in terms of averaged scalar values, such as is typically measured by experiments on liquid suspensions or solutions. In particular, when the chromophore molecules are incorporated into a polymer, the structure can impose constraints on the orientation of chromophores and at least some correlation between the orientation of a particular chromophore, and its near neighbours that make significant contributions to the field it experiences, is to be expected. In the idealised case, chromophores can be modelled as located on a regular lattice with only a small number of discrete orientations allowed. The vector components of the local field can in this situation only be properly modelled by combining individual tensor components in a full tensor description of the mutual polarisation process.

The purpose of this paper is to present a method for solving a quadratic tensor equation for the dipole moment due to both an external field and mutual polarisation, and hence the effective polarisabilities in a bulk medium up to the first hyperpolarisability. No linearisation of the equations is done, and all tensor components are incorporated throughout. The method can be extended to higher order tensor equations and hyperpolarisabilities in a straightforward if tedious manner.

From the effective polarisabilities the corresponding susceptibilities can be calculated by simple summation.

The calculation of dipole interactions in molecular crystals has received extensive attention in the research literature, as reviewed for example by Munn ⁽⁹⁾. This paper concentrates on only one aspect of this broad field, namely on finding a tensor solution to the non-linear equation for induced polarisabilities. In this spirit, the next section gives only a brief account of the origin of this non-linear equation; more details on the many ramifications of this subject can be found in the references. Section 3 presents the scalar solution in analytic form, both in order to establish relevant variables and to supply a basis of comparison with the iterative tensor solution that is the subject of section 4.

2. Problem formulation

The molecular polarisabilities are defined by the dipole moment \mathbf{P} induced by the electric field \mathbf{E} in which it is immersed:

$$\bar{P} = \bar{P}^0 + \bar{\alpha} \cdot \bar{E} + \frac{1}{2} \bar{\beta} : \bar{E}\bar{E} + \dots \quad (1)$$

Here tensors are decorated by dots to indicate their rank - α is a matrix, β a 3rd rank tensor - and the dyadic double dot product ($:$) is defined in tensor notation by

$$(\bar{\mathbf{A}}:\bar{\mathbf{B}}\bar{\mathbf{C}})_{jk}^i = \mathbf{A}_{mn}^i \mathbf{B}_j^n \mathbf{C}_k^m \quad (2)$$

where the standard convention of summing over repeated tensor indices is assumed. In a bulk material, the local field \mathbf{E} experienced by \mathbf{P} is composed of the external field \mathbf{E}^0 and contributions \mathbf{E}_i from its neighbours \mathbf{P}_i :

$$\bar{\mathbf{E}} = \bar{\mathbf{E}}^0 + \sum \bar{\mathbf{E}}_i \quad (3)$$

In a liquid or other disordered system, substitution of equation (3) into (1) and expressing the \mathbf{E}_i in terms of \mathbf{P}_i , leads to a set of coupled non-linear equations for the \mathbf{P}_i . However, in a system, which is ordered at least locally over the spatial range of the dipole field, one can use the ordering to reduce it to a single equation. In a simple regular lattice formed e.g. by an idealised isotactic polymer, all dipoles are equal by symmetry. More generally, we assume that there may be more than one discrete set of dipoles, but that the moments in set I are related to that of P by a relation $\mathbf{P}_i = \mathbf{S}_i \mathbf{P}$ where \mathbf{S}_i is a fixed and known matrix that represents a symmetry operation (e.g. rotation or reflection with or without scaling). This could arise, for example, in a syndiotactic polymer where every second chromophore is rotated by a fixed angle.

The field experienced by the reference dipole \mathbf{P} due to its neighbours \mathbf{P}_i can hence be related to \mathbf{P} itself, by an expression for the dipole field factorised in terms of the Lorentz tensor \mathbf{L} :

$$\bar{\mathbf{E}}_i = f_i \ddot{\mathbf{L}}_i \cdot \ddot{\mathbf{S}}_i \cdot \bar{\mathbf{P}} \quad (4)$$

Choosing the origin of the coordinate system at the position of \mathbf{P} and using the standard expression for the dipole field, the factors f and L are given by explicit expressions of the form:

$$f_i = \frac{3}{4\pi\epsilon_0 r_i^3} \quad \ddot{\mathbf{L}}_i = \left[\frac{\vec{r}_i \vec{r}_i}{r_i^2} - \frac{1}{3} \mathbf{I} \right] \ddot{\mathbf{p}} \quad (5)$$

The Lorentz matrix \mathbf{L} determines the vector components of the field while the scalar factor f_i carries the dependence on spatial separation. Since in a typical polymer the chromophore dimensions may be comparable to the dipole separation, use of the dipole approximation is not strictly justified and this may to some extent be compensated for by modifying the short distance behaviour of f_i , as investigated in a subsequent paper.

For the purposes of the derivation presented here, the detailed functional forms of the factors are unimportant but it is noted that by combining equations (3) and (4) the local field acting on \mathbf{P} is determined by a field factor matrix \mathbf{F} defined by

$$\sum \bar{\mathbf{E}}_i = \left[\sum_i f_i \ddot{\mathbf{L}}_i \cdot \ddot{\mathbf{S}}_i \right] \cdot \bar{\mathbf{P}} \equiv \ddot{\mathbf{F}} \cdot \bar{\mathbf{P}} \quad (6)$$

In a linear polymer chain or for a thin layer of such molecules, the convergence of the sum in the definition of the field factor matrix is not problematic since the dipole field drops off as $1/r^3$ at large distances, so that only near neighbours need to be included in the sum. In a bulk material, on the other hand, the sum formally has a logarithmic divergence and more sophisticated methods are needed to deal with this. This problem has been extensively studied, e.g. in the work of Tomasi et al ⁽¹⁰⁾ and references contained therein, where the far field contribution is represented by introducing an appropriate surface charge distribution on the boundary of a cavity surrounding the molecule. In this paper, we are not concerned with the details of calculating the field

factor and concentrate on a technique for calculating the induced dipole moment self-consistently once \mathbf{F} is known.

Substituting (6) into (1) the dipole moment \mathbf{P} as a result of both an external field \mathbf{E}^0 and local field effects are then to be found by solving the single quadratic tensor equation

$$\begin{aligned} \bar{\mathbf{P}} = \bar{\mathbf{P}}^0 + (\bar{\alpha}^0 \cdot \bar{\mathbf{F}}) \cdot \bar{\mathbf{P}} + \frac{1}{2}(\bar{\beta}^0 : \bar{\mathbf{F}}\bar{\mathbf{F}}) : \bar{\mathbf{P}}\bar{\mathbf{P}} + \bar{\beta}^0 : (\bar{\mathbf{F}} \cdot \bar{\mathbf{P}})\bar{\mathbf{E}}^0 + \\ + \bar{\alpha}^0 \cdot \bar{\mathbf{E}}^0 + \frac{1}{2}\bar{\beta}^0 : \bar{\mathbf{E}}^0\bar{\mathbf{E}}^0 \end{aligned} \quad (7)$$

Here use has been made of the fact that β is symmetric in its covariant indices allowing interchange of the factors in the double dot product. The superscripts 0 have been added to the polarisability tensors to emphasise the fact that as with \mathbf{P}^0 they refer to the properties of the isolated molecule.

Once again, the calculation of these intrinsic hyperpolarisabilities is for the purpose of this article considered to be a solved problem; it is by no means trivial, and a vast literature exists describing sophisticated methods such as the Time Dependent Hartree-Fock method (TDHF) proposed by Karna and Dupuis⁽¹¹⁾. However, our concern here is to solve equation (7) for the induced dipole moment \mathbf{P} , in the form of a tensor ‘‘power series’’ in the external field similar in form to equation (1), in such a way that the induced hyperpolarisabilities can be expressed in terms of known intrinsic molecular hyperpolarisabilities.

3. Scalar solution

It is instructive to first consider the solution of equation (7) in the scalar approximation where all tensor products become ordinary arithmetic products. In that case equation (7) reduces to a quadratic equation in the scalar variable P and its solution can be written down directly:

$$P = \frac{1}{\beta^0 F^2} [1 - \alpha^0 F - \beta^0 F^2 E^0 + \sqrt{1 - 2\alpha^0 F - 2\beta^0 F E^0 + \alpha^{0^2} F^2 - 2\beta^0 F^2 P^0}] \quad (8)$$

The appropriate sign for the square root has been selected to obtain the correct form in the limit $\beta \rightarrow 0$ where equation (1) becomes linear, namely

$$P \rightarrow \frac{P^0 + \alpha^0 E^0}{1 - \alpha^0 F} \quad (9)$$

which is the well-known result for linear response, that the effect of the local field is a mutual depolarisation factor $1/(1-\alpha F)$ which modifies both the intrinsic dipole moment and the linear polarisability. To extend this to the non-linear case, we expand the root expression in equation (8) as a power series in E^0 , keeping terms to second order. This leads in a natural way to the definition of depolarisation factors defined as $d=P/P^0$, $a=\alpha/\alpha^0$, and $b=\beta/\beta^0$ for the dipole moment, polarisability and hyperpolarisability respectively, i.e. equation (8) expands into the form

$$P = dP^0 + a\alpha^0 E^0 + \frac{1}{2}b\beta^0 E^{0^2} \quad (10)$$

The expressions for the depolarisation factors are reduced to a simple form by the introduction of the dimensionless variables

$$x_0 = \alpha^0 F \quad y_0 = \beta^0 F^2 P^0 \quad (11)$$

in terms of which the following expressions are obtained:

$$d = \frac{1 - x_0 - \sqrt{1 - 2x_0 + x_0^2 - 2y_0}}{y_0} \quad (12)$$

$$a = \frac{1}{x_0} \left[\frac{1}{\sqrt{1 - 2x_0 + x_0^2 - 2y_0}} - 1 \right] \quad (13)$$

$$b = \sqrt{(1 - 2x_0 + x_0^2 - 2y_0)^3} \quad (14)$$

Using plausible values for the free molecular polarisabilities and dipole magnitudes and separations, it is found that x_0 is a fraction of order 1 but $y_0 \ll x_0$. For future reference, it is noted that equations (12)-(14) can be expanded as power series in the factor $y_0/(1-x_0)^2$ as follows:

$$d = \frac{1}{1-x_0} + \frac{y_0}{2(1-x_0)^3} + \frac{y_0^2}{2(1-x_0)^5} + \frac{5y_0^3}{8(1-x_0)^7} + \frac{7y_0^4}{8(1-x_0)^9} + \dots \quad (15)$$

$$a = \frac{1}{1-x_0} + \frac{y_0}{x_0(1-x_0)^3} + \frac{3y_0^2}{2x_0(1-x_0)^5} + \frac{5y_0^3}{2x_0(1-x_0)^7} + \frac{35y_0^4}{8x_0(1-x_0)^9} + \dots \quad (16)$$

$$b = \frac{1}{(1-x_0)^3} + \frac{3y_0}{(1-x_0)^5} + \frac{15y_0^2}{2(1-x_0)^7} + \frac{35y_0^3}{2(1-x_0)^9} + \dots \quad (17)$$

Note that in the limit as $y_0 \rightarrow 0$, the depolarisation factors reduce to powers of $(1-x_0)^{-1}$. This is the scalar simplification of the expression usually referred to ⁽⁸⁾ as the “local field factor” and shows that the conventional proportionality of effective polarisabilities in a medium to powers of the local field factor, only holds when y_0 can be neglected. Putting $y_0 = 0$ amounts to the linear simplification referred to in the introduction, i.e. only the linear term is retained in equation (4) even though non-linear terms are retained in equation (1).

4. Solution of the Tensor Equation.

The scalar solution has shown that it is both important and simple to treat the first term that is linear in \mathbf{P} on the right hand side of equation (7) exactly, as this leads to the ubiquitous factor $(1-x_0)^{-1}$. We change equation (7) into a recursive form that incorporates this idea:

$$\begin{aligned} \bar{P}_n = (1 - \bar{\alpha}^0 \cdot \bar{\mathbf{F}})^{-1} \cdot [\bar{P}^0 + \frac{1}{2}(\bar{\beta}^0 : \bar{\mathbf{F}}\bar{\mathbf{F}}) : \bar{P}_{n-1} \bar{P}_{n-1} + \bar{\beta}^0 : (\bar{\mathbf{F}} \cdot \bar{P}_{n-1}) \bar{E}^0 + \\ + \bar{\alpha}^0 \cdot \bar{E}^0 + \frac{1}{2} \bar{\beta}^0 : \bar{E}^0 \bar{E}^0] \end{aligned} \quad (18)$$

The subscript n indicates the order of the recursion, which is started by defining the zeroth-order recursion as $\mathbf{P}_0 \equiv 0$. Further progress is facilitated by introducing a number of dimensionless vectors and tensors, in analogy to the variables in the scalar analysis.

Equation (11) shows that the magnitude of the intrinsic molecular dipole moment plays the role of a scaling constant. In order also to treat the case of molecules with

zero intrinsic moment using the same formalism, the scaling constant is reassigned by writing

$$\bar{P}^0 = P^0 \bar{p}^0; \quad \bar{p}^0 = \begin{cases} \bar{P}^0 / |\bar{P}^0| & \text{if } |\bar{P}^0| \neq 0 \\ \bar{0} & \text{otherwise} \end{cases} \quad (19)$$

While keeping P^0 as the magnitude of the moment of the isolated molecule for intrinsically polarised molecules, for unpolarised molecules any convenient value may be chosen, e.g. such that the external field is scaled to a dimensionless vector of order unity by the following transformation:

$$\bar{e} = (1/P^0) \ddot{\mathbf{F}}^{-1} \cdot \bar{E}^0 \quad (20)$$

The variables x and y of the scalar treatment now become dimensionless tensors:

$$\ddot{\mathbf{x}}_0 = \ddot{\alpha}^0 \cdot \ddot{\mathbf{F}} \quad \ddot{\mathbf{y}}_0 = P^0 \ddot{\beta}^0 : \ddot{\mathbf{F}}\ddot{\mathbf{F}} \quad (21)$$

In terms of these the defining relation for intrinsic molecular polarisabilities, equation (1), can be written as:

$$\bar{p} \equiv \bar{P}/P^0 = \bar{p}^0 + \ddot{\mathbf{x}}_0 \cdot \bar{e} + \frac{1}{2} \ddot{\mathbf{y}}_0 : \bar{e}\bar{e} \quad (22)$$

while equation (18) is transformed into

$$\bar{p}_n = \ddot{D} \cdot [\bar{p}^0 + \ddot{\mathbf{x}}_0 \cdot \bar{e} + \frac{1}{2} \ddot{\mathbf{y}}_0 : \bar{e}\bar{e} + \ddot{\mathbf{y}}_0 : \bar{p}_{n-1} \bar{e} + \frac{1}{2} \ddot{\mathbf{y}}_0 : \bar{p}_{n-1} \bar{p}_{n-1}] \quad (23)$$

where for convenience the definition of the dimensionless matrix $\mathbf{D} \equiv (1 - \mathbf{x}_0)^{-1}$ was introduced.

Conceptually, what needs to be done is to solve equation (23) for the vector \mathbf{p}_n as a function of \mathbf{e} and expand this as a power series in \mathbf{e} (the process that was explicitly performed in the scalar case). If the end result can be expressed in the same functional form as equation (22), namely

$$\bar{\mathbf{p}}_n = \bar{\mathbf{w}}_n + \bar{\mathbf{x}}_n \cdot \bar{\mathbf{e}} + \frac{1}{2} \bar{\mathbf{y}}_n : \bar{\mathbf{e}} \bar{\mathbf{e}} \quad (24)$$

the coefficients in equation (24) clearly would represent the effective polarisabilities in the medium. The first iteration of equation (23) using $\mathbf{p}_0=0$ is already in this form, and allows the identifications

$$\bar{\mathbf{w}}_1 = \bar{\mathbf{D}} \cdot \bar{\mathbf{p}}^0 ; \quad \bar{\mathbf{x}}_1 = \bar{\mathbf{D}} \cdot \bar{\mathbf{x}}_0 ; \quad \bar{\mathbf{y}}_1 = \bar{\mathbf{D}} \cdot \bar{\mathbf{y}}_0 \quad (25)$$

Using equations (24) and (25) we can simplify equation (23) to read

$$\bar{\mathbf{p}}_n = \bar{\mathbf{p}}_1 + \frac{1}{2} \bar{\mathbf{y}}_1 : [2\bar{\mathbf{p}}_{n-1} \bar{\mathbf{e}} + \bar{\mathbf{p}}_{n-1} \bar{\mathbf{p}}_{n-1}] \quad (26)$$

To obtain the solution of equation (26) in the desired functional form, \mathbf{p}_n on the left and \mathbf{p}_{n-1} on the right hand side is substituted from equation (24). The resulting tensor products on the right have to be rearranged to move all factors \mathbf{e} to the right, in the appropriate single or double dot products as required by the form of equation (24). This transformation is non-trivial, but can be accomplished by using the fact that \mathbf{y} is

a symmetric tensor, as well as the following identities, all of which are easily proven by using equation (2) and analogous component expansions:

$$\begin{aligned}
\ddot{\mathbf{A}}:\bar{\mathbf{B}}\bar{\mathbf{C}} &\equiv (\ddot{\mathbf{A}} \cdot \bar{\mathbf{B}}) \cdot \bar{\mathbf{C}}; \quad \ddot{\mathbf{A}}:\bar{\mathbf{B}}\ddot{\mathbf{C}} \equiv (\ddot{\mathbf{A}} \cdot \bar{\mathbf{B}}) \cdot \ddot{\mathbf{C}} \\
\ddot{\mathbf{A}}:\bar{\mathbf{B}}(\ddot{\mathbf{C}} \cdot \bar{\mathbf{D}}) &\equiv (\ddot{\mathbf{A}}:\bar{\mathbf{B}}\ddot{\mathbf{C}}) \cdot \bar{\mathbf{D}} \\
\ddot{\mathbf{A}}:(\bar{\mathbf{B}} \cdot \bar{\mathbf{C}})\bar{\mathbf{D}} &\equiv (\ddot{\mathbf{A}} \cdot \bar{\mathbf{B}}):\bar{\mathbf{C}}\bar{\mathbf{D}} \\
\ddot{\mathbf{A}}:\bar{\mathbf{B}}(\ddot{\mathbf{C}} \cdot \bar{\mathbf{D}}\bar{\mathbf{E}}) &\equiv (\ddot{\mathbf{A}}:\bar{\mathbf{B}}\ddot{\mathbf{C}}):\bar{\mathbf{D}}\bar{\mathbf{E}} \equiv [(\ddot{\mathbf{A}} \cdot \bar{\mathbf{B}}) \cdot \ddot{\mathbf{C}}]:\bar{\mathbf{D}}\bar{\mathbf{E}}
\end{aligned} \tag{27}$$

Comparing coefficients of each order in \mathbf{e} in the rearranged version of equation (26) and only keeping terms up to 2nd order to stay consistent with the truncation of equation (1), the following set of recursion relations is obtained:

$$\bar{\mathbf{w}}_n = \bar{\mathbf{w}}_1 + \frac{1}{2}\ddot{\mathbf{Y}}_1:\bar{\mathbf{w}}_{n-1}\bar{\mathbf{w}}_{n-1} \tag{28}$$

$$\ddot{\mathbf{x}}_n = \ddot{\mathbf{x}}_1 + \ddot{\mathbf{Y}}_1 \cdot \bar{\mathbf{w}}_{n-1} + \ddot{\mathbf{Y}}_1:\bar{\mathbf{w}}_{n-1}\ddot{\mathbf{x}}_{n-1} \tag{29}$$

$$\ddot{\mathbf{y}}_n = \ddot{\mathbf{y}}_1 + 2\ddot{\mathbf{Y}}_1 \cdot \ddot{\mathbf{x}}_{n-1} + \ddot{\mathbf{Y}}_1:\ddot{\mathbf{x}}_{n-1}\ddot{\mathbf{x}}_{n-1} + (\ddot{\mathbf{Y}}_1 \cdot \bar{\mathbf{w}}_{n-1}) \cdot \ddot{\mathbf{y}}_{n-1} \tag{30}$$

Equations (28)-(30), together with (25), form the key set of equations that allows one to proceed directly from a known set of intrinsic molecular polarisabilities as contained in \mathbf{p}_0 , \mathbf{x}_0 and \mathbf{y}_0 , to the induced polarisabilities for the bulk medium in an external field that is embodied in $\bar{\mathbf{w}}_n$, \mathbf{x}_n and \mathbf{y}_n . The latter are by construction iterative approximations to the underlying material properties for which the obvious notation is \mathbf{w} , \mathbf{x} and \mathbf{y} . The recursion has a hierarchical structure: first equation (28) can be iterated to the desired degree of accuracy, then the results of this are used to iterate equation (29), and in turn the results from both of these are needed to iterate equation (30).

To regain the physical polarisation tensors from the dimensionless forms, \mathbf{e} is substituted from equation (20) into (24) and by comparison with equation (1) the induced or effective polarisabilities are given by

$$\bar{P}^i = P^0 \bar{w} \quad (31)$$

$$\bar{\alpha} = \bar{\mathbf{x}} \cdot \bar{\mathbf{F}}^{-1} \quad (32)$$

$$\bar{\beta} = \frac{1}{P^0} \bar{\mathbf{y}} : \bar{\mathbf{F}}^{-1} \bar{\mathbf{F}}^{-1} \quad (33)$$

where P^i represents the modified intrinsic moment as a result of local fields but in the absence of an external field.

The claim that the iterative solution presented here is equivalent to an analytical solution, can be confirmed by noticing that when equations (31-33) are reduced to scalar equivalents, they imply the following relationships to the depolarisation factors introduced in section 3:

$$d = w \quad ; \quad a \equiv \alpha/\alpha^0 = x/x_0 \quad ; \quad b \equiv \beta/\beta^0 = y/y_0 \quad (34)$$

When the scalar equivalents of the tensor recursions in equations (28-30) are performed algebraically by repeated substitution, it is easily seen that power series are generated which are identical to those of equations (15-17). Moreover, this comparison gives information about the convergence of the iteration. It is observed that in the n^{th} iteration of equations (28) and (29), all terms up to the $(n-1)$ th order in $y_0/(1-x_0)^2$ are correct, while in the case of equation (30) correct terms up to order $(n-2)$

are obtained. As this observation reflects the numerical coefficients in the expansion, it can be transferred also to the case of the tensor recursion to give a guideline for truncating the iteration.

The iterative solution has an important advantage over the analytical one, in that it applies also to higher order optical constants. For example, if the second order hyperpolarisability term is also included in equation (1), even for the scalar case the calculation of induced optical constants from the resulting cubic equation becomes very complicated. The extension of the iterative solution to this case is by contrast straightforward, although tedious in performing the tensor algebra corresponding to equation (27).

Returning to the case of the quadratic tensor equation, it is noted that the concept of a depolarisation factor is not useful beyond the linear polarisation term in this case. The reason is demonstrated by equation (34): while \mathbf{x}_0 is still a matrix and can be inverted to define a depolarisation matrix \mathbf{a} , \mathbf{y}_0 is a 3rd rank tensor and cannot be inverted to produce a tensor equivalent of \mathbf{b} . However, this is of no consequence since equation (33) gives a well-defined prescription for finding the induced hyperpolarisability.

In principle, also for the tensor case the recursions in equations (28-30) could be done algebraically by repeated substitution. However, in order to avoid the accumulation of involved tensor products it was found more practical to apply the equations numerically. Since the result of the tensor products on the right hand sides always return a tensor of the appropriate rank as specified by the left hand side, subsequent iterations do not increase in complexity provided that the results of previous iterations are stored for reuse.

Finally, we consider the calculation of macroscopic susceptibilities. Substituting back the solutions of equations (28-30) into equation (24) gives an expression for the induced molecular dipole moment, which only depends explicitly on the external field, and can be summed over all dipoles in a suitably chosen unit cell to give the polarisation of the medium. Assuming that the external field is homogeneous on an atomic scale, it can be factored out of the sums on the right hand side and using the conventional factors in the definition⁽⁸⁾ of the n^{th} order susceptibility tensor χ^n , we get

$$\ddot{\chi}^n = \ddot{\alpha}_c^n / n! \epsilon_0 V \quad (35)$$

Here V is the volume of the unit cell, which is chosen large enough to contain a representative collection of molecular orientations and the cellular total of the n^{th} polarisability is given by

$$\ddot{\alpha}_c^1 = \ddot{\alpha} + \sum_j \ddot{\mathbf{S}}_j \cdot \ddot{\alpha} \cdot \ddot{\mathbf{S}}_j^{-1} ; \ddot{\alpha}_c^2 = \ddot{\beta} + \sum_j \ddot{\mathbf{S}}_j \cdot \ddot{\beta} \cdot \ddot{\mathbf{S}}_j^{-1} \ddot{\mathbf{S}}_j^{-1} \quad (36)$$

The first term in each of these equations refer to the polarisability of the molecule or chromophore at the origin which defines the coordinate system in which the tensors are determined, and the sum over j extends over all other chromophores in the unit cell. Note that for chromophore j its polarisability is given by an equation like equation (1), but in its own coordinate system; i.e., the effective external field it experiences is $\mathbf{S}_j^{-1} \mathbf{E}$. From this consideration the factors \mathbf{S} in equation (36) are derived.

5. Conclusions

The conceptual framework for this study was the case of identical highly polarisable and anisotropic molecular chromophore molecules, embedded in a regular lattice formed e.g. by a polymer backbone. In this case it was shown that mutual polarisation of the chromophores with or without an external electric field, is determined by a single tensor equation, which is non-linear in the molecular dipole moment. The equation includes non-linearity in the external field as well as non-linearity of the local field in terms of higher order polarisabilities. By rewriting this equation in a recursive form, it was shown that it can be solved iteratively in a way that directly expresses the induced (effective) polarisability tensors of a molecule as a result of both the external field and the mutual interactions, in terms of the intrinsic polarisabilities of an isolated molecule. From this the non-linear susceptibility tensors of the bulk medium can be calculated in a straightforward way. No tensor averaging is used, so that the interaction between different tensor components of neighbouring molecules is fully included.

The idea of using iteration to solve such a non-linear equation has also been pursued by other authors, e.g. in the work of Munn⁽⁹⁾ where a non-linear equation for the local field is solved in this manner. However, the advantage of the present formalism is that by eliminating the explicit appearance of the local field, the induced polarisabilities are directly expressed in terms of the intrinsic polarisabilities. Moreover, this is done by a set of recursion relations which are in themselves exact solutions of the non-linear equation (as demonstrated by the fact that they give rise to the same infinite power series as the analytical solution, for the scalar case). Although iteration of the recursion relations also needs to be truncated in practice, the truncation order can be

decided purely on the grounds of the intrinsic polarisabilities and is not related to truncation of the expansions in orders of the electric field.

The derivation presented only included terms up to the first hyperpolarisability, i.e. 2nd order susceptibility. However, the method used allows a straightforward extension to higher order non-linearity.

Representing an optical polymer as a regular lattice, is certainly a highly idealised abstraction. However, in most of the derivation only limited use was made of this assumption. To reduce the problem from coupled equations in a disordered material to a single equation as in (7), it is only necessary to have a local ordering where the neighbours (within range of the dipole field) of a given chromophore have fixed (but not necessarily identical) orientations and positions. Under this much more realistic assumption, the resulting equation is solved essentially exactly, depending on the number of iterations performed. Only at the very last step of finding bulk properties, was the concept of a repetitive unit cell invoked, implying a long range ordering as well. This assumption could be relaxed without affecting the rest of the derivation by assuming such unit cells to be uncorrelated and doing a statistical average over different unit cell orientations. This idea is left for future work as the present focus is on describing the local effects as accurately as possible.

Finally, it is remarked that the equations presented are quite practical for numerical calculations, with all matrices and tensors in 3-space so that relatively small numbers of components are involved. This is to be further demonstrated in the subsequent article in this series where a practical application to calculations for specific chromophore molecules of the type mentioned in the introduction is presented.

Supporting Information Available: The calculations were implemented in the form of worksheets for the MathCAD program, and examples of these have been deposited as supporting information and is available free of charge via the internet from the ACS website (<http://pubs.acs.org>).

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