Polish J. Chem., **76**, 155–165 (2002) **REVIEW ARTICLE**

Local Fields and Distributed Response: Electric Susceptibility Calculations for Molecular Materials*

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(Received June 27th, 2001)

Progress in the last 25 years towards realistic theoretical calculation of linear and non-linear electric susceptibilities of molecular materials is reviewed. Key issues are proper treatment of local electric fields and of the spatial distribution of molecular response. The local fields contribute directly to the susceptibilities and indirectly by modifying the molecular response in the material. Distributing molecular dipolar response over equivalent submolecules gives good results if enough submolecules are used. Fully distributed response including charge transfer within molecules can approach experimental accuracy.

Key words: molecular materials, distributed molecular response, hyperpolarizability, local field, non-linear optics

1. Introduction

Quantitative microscopic theories of linear and non-linear electric and optical susceptibilities of molecular materials are important for interpreting and controlling a range of material properties, many of practical significance. Relevant properties include refraction and non-linear effects such as second-harmonic generation; intensities of lattice vibrational spectra and electro-absorption spectra; and charge-carrier generation, transport and trapping. Aspects of the necessary theory were reviewed some years ago [1].

Since that time, significant progress has been made in two areas. The role of the local electric field induced by an external applied electric field has long been recognized as essential to treatments of electric susceptibilities in molecular materials. It has also long been recognized that molecules respond to the local field through *effective* polarizabilities and hyperpolarizabilities appropriate to the material environment. One important factor that makes the effective response differ from that of the free molecule is the local field due to the permanent charge distributions of neigh-

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*Dedicated to the memory of Professor Krzysztof Pigoń.

bouring molecules in the material, and calculations of this field and its effect on response are now becoming available.

Secondly, in 1976 Luty recognized the importance of going beyond the treatment of molecules as single points [2]. Instead, he introduced the idea of chemically equivalent point *submolecules* over which the molecular polarizability is equally distributed. This approach was then extended to polycyclic aromatic molecular crystals, where it was shown to suppress unphysical negative polarizabilities required to fit a point-molecule treatment to experiment [3].

The submolecule approach has proved tractable and yields physically realistic results by taking account of the spatial variation of the local field over molecules. However, it relies on what may be an arbitrary choice of submolecules. Moreover, it cannot take explicit account of charge redistribution within molecules in an electric field: even a uniform electric field implies a constant potential gradient that drives charge flow. Handling such *distributed response* requires a generalized treatment such as that presented by Stone [4]. A tractable implementation of this treatment using the topological Atoms-in-Molecules method has been applied to the polarizability of isolated molecules [5], and has been extended to the water dimer [6] and to non-linear response in molecular crystals [7].

The present article reviews the present state of knowledge in theoretical interpretation and prediction of linear and non-linear electric susceptibilities in molecular materials. We emphasize the role of permanent electric fields in modifying the molecular response in the material environment, and the treatment of distributed molecular response. We present not only a systematic account of previous work but also some new examples. We stress applications of theory rather than the theory itself.

2. Local Fields and Susceptibilities

In this section, we summarize the basic theory required to treat the local field induced by an external field and the susceptibilities of a molecular material. Our concern will be results rather than derivations available elsewhere [1]. We begin with a crystal in a point-molecule treatment; although a major concern is the effect of distributed response, this does not alter the basic algebraic theory. The theory is also readily extended to disordered materials.

The crystal has Z molecules labelled k in the unit cell, with polarizabilities α_k and first and second hyperpolarizabilities β_k and γ_k. All response coefficients have a frequency dependence, which will not be written explicitly. The local electric field at molecule k is $\mathbf{F}_k$, which for linear response is related to the usual macroscopic electric field $\mathbf{E}$ by

$$\mathbf{F}_k = \mathbf{d}_k \cdot \mathbf{E} \tag{1}$$

Here $\mathbf{d}_k$ is the local-field tensor, given by

$$\mathbf{d}_k = \sum_{k'} (\mathbf{I} - \mathbf{L} \cdot \mathbf{a})^{-1}_{kk'} \equiv \sum_{k'} \mathbf{D}_{kk'} \tag{2}$$

where **I** is the $3Z$ unit matrix, **L** is the $3Z$ matrix of the Lorentz factor tensors $\mathbf{L}_{kk'}$ obtainable from the crystal structure [8], and **a** is the block-diagonal $3Z$ matrix of the reduced polarizabilities $\mathbf{a}_k = \alpha_k/\varepsilon_0 v$, with v the unit-cell volume. The linear electric susceptibility follows as

$$\chi^{(1)} = \sum_k \mathbf{a}_k \cdot \mathbf{d}_k = \sum_{kk'} (\mathbf{a}^{-1} - \mathbf{L})^{-1}_{kk'} \tag{3}$$

which shows how the refractive indices can be calculated given the polarizabilities and the crystal structure.

For non-linear response, the local field also becomes non-linear. However, the susceptibilities can still be expressed in terms of the previous local-field tensor. The quadratic susceptibility is [9]

$$\chi^{(2)} = \sum_k \tilde{\mathbf{d}}_k \cdot \mathbf{b}_k : \mathbf{d}_k \mathbf{d}_k \tag{4}$$

where $\mathbf{b}_k = \beta_k/\varepsilon_0 v$. The cubic susceptibility $\chi^{(3)}$ is the sum of a *direct* term

$$\chi^{(3d)} = \sum_k \tilde{\mathbf{d}}_k \tilde{\mathbf{d}}_k : \mathbf{c}_k : \mathbf{d}_k \mathbf{d}_k \tag{5}$$

where $\mathbf{c}_k = \gamma_k/\varepsilon_0 v$, and a *cascading* term

$$\chi^{(3c)} = \hat{I} \sum_{kk'k''} \tilde{\mathbf{d}}_k \tilde{\mathbf{d}}_k : \mathbf{b}_k \cdot \mathbf{D}_{kk'} \cdot \mathbf{L}_{k'k''} \cdot \mathbf{b}_{k''} : \mathbf{d}_{k''} \mathbf{d}_{k''} \tag{6}$$

where the operator $\hat{I}$ generates all distinct terms by interchanging different frequencies [9,10]. The quadratic susceptibility is zero in centrosymmetric materials in the dipole approximation, but if the molecules are non-centrosymmetric their first hyperpolarizability can make a significant contribution to the cubic susceptibility through the cascading term. We shall not consider here effects that go beyond the dipole approximation to yield bulk [11] or surface [12,13] quadratic response in centrosymmetric crystals.

For disordered materials, these expressions can be applied directly with the crystal unit cell replaced by a simulation box. Appropriate averaging is then applied. This approach has the advantage that the Ewald sum implicit in the Lorentz-factor tensors provides a rigorous and efficient treatment of long-range dipole interactions [14]. We do not consider here any cavity treatment of local fields.

3. Permanent Local Fields and Molecular Response

Admitting non-linear molecular response yields non-linear material response. It also yields linear molecular response that depends on the electric field, and in the material environment such a field is provided by the permanent charge distributions of the surrounding molecules. Thus even in treating linear material response one needs the molecular polarizability evaluated at the relevant permanent local field $\mathbf{F}^{\mathrm{p}}$. For a crystal in which the molecules have effective dipole moments μ_k, this field is given by [15]

$$\mathbf{F}_k^p = \sum_{k'} \mathbf{L}_{kk'} \cdot \mu_{k'} / \varepsilon_0 \nu \tag{7}$$

where it is assumed that there is no bulk crystal dipole moment [16].

This approach was first applied to the HCN crystal [15]. Equation (7) giving the permanent field in terms of the dipole moment was solved simultaneously with quantum chemical calculations of the dipole moment in a finite field. The effect on the polarizability was reported to be small. Later the extension of the approach to non-linear response was described [17] but not implemented numerically. Eventually, a detailed numerical treatment was given for the linear, quadratic and cubic susceptibilities in the urea crystal [18]. The effective dipole moments required to calculate the permanent field from Eq. (7) are given by [16]

$$\mu_k = \sum_{k'} \widetilde{\mathbf{D}}_{kk'} \cdot \mu_{k'}^0 \tag{8}$$

where μ_k^0 is the zero-field dipole moment. The local-field tensor is to be calculated using the effective polarizability at the permanent field. This is approximated by its value calculated at zero field, which gives a first estimate of the permanent field *via* Equations (7) and (8). The quantum-chemical calculations are then repeated, after which the procedure had converged for urea. It was also found that the demanding high-level calculations needed to be performed only once, since the zero-field first and second hyperpolarizabilities gave an adequate description of the field dependence of the polarizability up to the permanent field. The numerical results showed rather little effect of the permanent field on the polarizability and linear susceptibility (as in HCN), with good agreement with the experimental refractive indices. The effect on the first hyperpolarizability was very large, with some components doubling in magnitude and changing in sign. However, a fortuitous cancellation led to much smaller effects on the quadratic susceptibility. For second-harmonic generation, this agreed well with experiment for SCF calculations, but these gave refractive indices that were too small. Once electronic correlation was included at the MP2 level, the quadratic susceptibility was too large by a factor of nearly 2, while the experimental refractive indices were nearly quantitatively reproduced.

An alternative approach [19] has been to calculate the linear and quadratic susceptibilities of urea crystal from first principles quantum-mechanical theory, using band theory with the Kohn–Sham local density approximation. This method is based on the determination of single-electron wave functions in a plane wave basis using the pseudopotential approach. Local-field effects associated with the linear response are incorporated by an iterative method [20], and the non-linear response is calculated using sums over a large number of eigenstates determined by diagonalization in the plane-wave basis. The results for the refractive indices of the urea crystal were too low compared with experiment, while the second-harmonic response was in good agreement with experiment, if the revised value [21] for the reference standard value of potassium dihydrogen phosphate (KDP) was used rather than that in the original experimental report [22]. The calculated susceptibility components, including local-field effects, were $\chi_{aa} = 2.0$, $\chi_{cc} = 2.3$, and $|\chi_{abc}| = 2.2$ pm/V, at $\lambda \to \infty$. These agree very well with those reported previously at the SCF level [18], namely $\chi_{aa} = 2.0$, $\chi_{cc} = 2.1$, and $|\chi_{abc}| = 2.1$ pm/V at $\lambda = 632.8$ nm for the electro-optic Pockels effect, even though effects due to hydrogen bonding and large inter-cell charge transfer neglected in the approach of Ref. [18] are stated [19] to be large and should therefore make the band theory approach superior.

This good agreement in the predicted susceptibilities suggests that the two methods may generally be of comparable quality for molecular crystals. If so, attempts to go beyond the self-consistent field approach, shown to be important as in urea as well as in many cases considered so far at the level of single-molecule response plus intermolecular electric field interactions, will probably be easier in the single-molecule response approach than in the band theory approach, where such attempts lead to high computational costs [23]. Note that the term “local field” has slightly different meanings in the two approaches: in the single-molecule response approach it is a Lorentz-type local field at a specific point in space where the molecules are assumed to be located, although calculated more accurately using a discrete approach instead of a continuous polarization [1], while in the band theory it represents a spatially varying potential acting in a distributed way throughout the unit cell [24]. It should be mentioned finally that, unlike the single-molecule response approach, the density functional approach using band theory is applicable also to covalent crystals, with which indeed the majority of reported calculations have been concerned [25].

As already mentioned, the methods described in Section 2 can also be applied to disordered materials, if a pseudo-ordered structure is assumed, where a simulation box is repeated to fill three-dimensional space. Such models have been used to calculate the linear and non-linear susceptibilities of pure liquids, namely benzene [14,26], nitrobenzene [27] and water [26]. A two-step approach was adopted in these calculations, where in the first step the structure of the liquid was calculated by standard molecular simulation techniques, and in the second step the response of the liquid to externally applied fields was calculated, thus allowing the extraction of macroscopic susceptibilities. The use of partial charges in the structure calculations to simulate the intermolecular electrostatic interactions made it possible to predict the distribution of permanent local fields in the liquid.

The method was introduced for liquid benzene [26]; different strategies to extract the susceptibilities were compared and found to be in good agreement, and the predicted values were compared with those resulting from a standard Lorentz local-field factor approach, which was shown to yield a slightly worse agreement with experiment. Later, the hyper-Rayleigh scattering depolarization ratio of liquid nitrobenzene was predicted [27]. It was found that the contribution of coherent scattering to the depolarization ratio is not negligible for the hyper-Rayleigh scattering signal of this system, and consequently should be taken into account generally for pure liquids. Although the permanent local fields were calculated in both liquids, no assessment of their influence on the molecular properties was made, nor was a possible molecular size effect taken into account. While the permanent local fields were relatively small and may not have large effects, and the size effect in benzene is small, as shown for the benzene crystal [28], the distribution of the molecular response for nitrobenzene using the submolecule approach described in the next section has a large effect on the crystal susceptibilities [29] and may therefore alter the predicted liquid response as well.

The molecular electric properties were calculated with moderately large basis sets and electronic correlation effects were taken into account, using Møller-Plesset theory at different levels. For all the liquids considered the electronic correlation effects were found to be quite large, especially on the non-linear properties. While in the first applications [27,28] only static properties were calculated, later dispersion effects were taken into account [26] and were found to have a large, non-negligible effect for both benzene and water.

That work emphasised the comparison of theoretical and experimental liquid susceptibilities free from any problems associated with the still unresolved question of the correct absolute values of the experimental reference standard [30], which generally complicates all comparisons between theoretical and experimental nonlinear susceptibilities. This was achieved by calculating the third-harmonic generation (THG) signal of liquid benzene and water, and comparing the ratio $\chi^{(3)}$(water)/$\chi^{(3)}$(benzene) with the experimental ratio. The prediction of the discrete local field model was compared with those of two continuum local field models, the Lorentz model and the Onsager model extended to non-linear optics by Wortmann and Bishop [31], which takes permanent local-field effects into account. The experimental gas-phase (hyper)polarizabilities and the refractive indices of the liquids (which are free from problems associated with experimental calibration standards) were very well reproduced, independent of the models employed in the case of the refractive indices. On the other hand, the predicted ratio $\chi^{(3)}$(water)/$\chi^{(3)}$(benzene) was rather poor compared with experiment, with the Onsager model yielding a value just inside the sizeable experimental error bars. Additionally, the predicted absolute $\chi^{(3)}$ values differed considerably between the discrete local field model and the extended Onsager model.

However, the assertion [31] that no cavity field factor involving the third-harmonic frequency 3ω appears in the expression connecting the cubic susceptibility with molecular properties has recently been called into question [32], essentially from the argument that such a factor *is* included in the presumably more accurate discrete field theory and should therefore appear in the extended Onsager model, too. If this factor is taken into account, the large difference between the $\chi^{(3)}$ values for the Onsager local-field model and the discrete local-field model in Ref. [26] essentially vanishes, but then the predicted ratio of the Onsager model becomes worse compared with experiment. One possible explanation for the discrepancies between theory and experiment may be large intermolecular charge-transfer effects on the second hyperpolarizability in water. Such CT and other non-electrostatic effects on the linear polarizability have been reported for water clusters [33] and for the water dimer [34], and although small, might be much larger for the hyperpolarizabilities. If relevant, these effects would probably also show up in ice isomorphs, and hence one possibility to check the importance of non-electrostatic interaction effects could be to perform DFT/band theory calculations on one of the ice polymorphs, for which predictions by the single-molecule response approach coupled with electrostatic interactions have been published [35].

4. Submolecules and Distributed Response

As noted in the Introduction, distributing dipolar response over submolecules allows apparently realistic effective polarizabilities to be derived from experimental linear susceptibilities. This treatment is reminiscent of distributed multipole analysis [36], which improves the convergence of electrostatic interactions by superimposing expansions about a set of atomic origins instead of a single molecular origin. Most early applications treated polycyclic aromatic molecules, with one submolecule per ring, and used the submolecule effective polarizability to provide a unified description of a range of crystal properties [1].

The effect of the choice of submolecules was seldom explored in early work. The primary aim was to obtain physically plausible polarizabilities for modest computational effort. These polarizabilities differed form those obtained from quantum chemistry, but this was to be expected because of environmental effects. Moreover, at that time polarizabilities from quantum chemistry had known deficiencies for these large molecules that made it unreasonable to use them to predict crystal refractive indices. The original submolecule treatment 25 years ago took the C–Cl fragments in hexachlorobenzene as submolecules [2]. Heavy atom (non-hydrogen) submolecules were used 25 years ago to treat local-field effects on spectra of doped anthracene crystals [37], and a little later it was found that for carbazole point rings gave rather unsatisfactory polarizabilities, so that the heavy atoms were taken as submolecules [38].

The quality of the submolecule treatment may also be gauged from the local fields calculated using the resulting polarizabilities. Calculations for acetanilide ($PhNHCOCH_3$) gave a local field tensor component along the crystal *a* axis that was less than unity [16], when values nearer 1.5 are more usually found. This work treated the phenyl ring as one submolecule and the remaining heavy atoms as the others. Subsequent work with different choices of submolecules shows that the unusually small local-field component is essentially independent of the detailed representation of the side chain but assumes a more reasonable value of about 1.4 once all carbon atoms in the phenyl ring are treated as submolecules [39]. At the same time, the components in the other crystallographic directions reduce from about 1.7 to 1.6.

More recently, developments in the techniques of quantum chemistry and increasing computer power have made it possible to calculate molecular polarizabilities in good agreement with experiment for isolated molecules. It has therefore become reasonable to see how well such high-level calculations predict crystal refractive indices, which again raises the question of how to represent the molecule in the crystal. The treatment for urea crystal, treated both at the atomic and the molecular level, has already been described, and has shown that in this case the distribution of the molecular response over the heavy atoms has only a small effect on the calculated susceptibilities [18]. The same was found for the benzene crystal [28]. A systematic study, extending to non-linear response, has been reported for naphthalene, anthracene and *meta*-nitroaniline (mNA) [40]. The molecular response properties were calculated with density functional theory, using specially designed basis sets for the calculation of hyperpolarizabilities [41] and, for comparison, at the SCF and correlated second-order Møller-Plesset (MP2) level, using a standard 6-31++G** basis set. This work allowed comparison with early work treating the aromatic hydrocarbons as point rings, as already mentioned, and with work on mNA for non-linear optics [42]. For the aromatic hydrocarbons, treating all heavy atoms as submolecules gave refractive indices in satisfactory agreement with experiment. For mNA, treating all heavy atoms as submolecules was essential even to give the correct ordering for the refractive indices. Treating the molecule as one point or three points gave the refractive index along *c*-axis as largest, when experimentally it is the smallest. The work on mNA also took account of permanent electric field effects. These are not large in the refractive indices, but were quite large for the first hyperpolarizabilities and only the inclusion of these effects led to second-order susceptibilities $\chi^{(2)}$ that were in reasonably good agreement with experimental values.

5. Charge Flow and Molecular Response

The treatments described so far have two shortcomings. The first is that the effect of the permanent electric field on molecular response is calculated by subjecting the molecule to a uniform field that is the average permanent field over the atoms or submolecules. Since the spatial variation of electric field in the crystal is very large, this treatment is questionable. The second shortcoming is that the treatment allows dipolar response within atoms or submolecules but not charge flow between them. Since even a uniform electric field corresponds to a linear gradient of electric potential that drives charge flow, including charge flow would seem desirable. Such response is necessarily distributed over the molecule.

Distributed response of all orders of multipole moment to all orders of potential gradient can be treated systematically [4]. Implementation then requires a suitable definition of atomic or other regions and what can be rather demanding integrations over the regions so defined. For this purpose, the topological Atoms-in-Molecules method was found to be tractable and to yield results that do not change markedly with basis set [5]. The first application to a molecular crystal was for urea [7], where comparison with experiment was complicated because the treatment did not include correlation. For linear response, the distributed response gave modest increases over the values without correlation. Assuming that the inclusion of correlation would have similar effects for distributed response and the usual dipolar response, the distributed response would again give good agreement with experiment. For the quadratic response, the effect of the distributed response was more marked and of a magnitude and sign sufficient to offset the over-estimate obtained from the usual dipolar responses when correlation was included.

A different approach to the same problem has recently been adopted [43]. Here a cluster of molecules is treated, with charge conserved within each molecule. The charge and dipole interactions are calculated explicitly and included in an INDO/S self-consistent computation in a suitable atomic basis. This allows charge flow within molecules and the development of atomic dipoles under the influence of the other molecules. The approach can also be used to supplement high-level calculations of the usual molecular polarizability. In this way, good predictions are obtained for the refractive indices of anthracene (with the greatest deviation in the largest component, as found in previous work [40]) and for perylene tetracarboxylic acid dianhydride (PTCDA). This work can be regarded as calculating the effective polarizability in the crystal environment, including charge flow. It then uses the polarizability separately to calculate the crystal properties. This avoids potential dangers in using cluster calculations to calculate crystal behaviour directly when there are long-range conditionally convergent dipole interactions to consider [44].

6. Conclusions

In this article, we have reviewed approaches developed over the last quarter century to calculate linear and non-linear electrical and optical susceptibilities for molecular materials. The materials discussed have been mainly ordered crystals, but key illustrations have also been drawn from disordered crystals and liquids. We have concentrated on our own work, but we have reported work by authors who have adopted approaches that rely on similar physical principles and find them effective.

The key factors in calculating these optical properties are as follows.

- Proper treatment of long-range electric fields in condensed matter.
- Inclusion of permanent electric field effects on molecular response.
- Distribution of response over molecules.
- Allowance for charge flow within molecules.

The response also needs to be calculated taking due account of correlation and frequency dependence.

Once these factors are all incorporated, the current evidence is that crystal and other condensed matter properties can be predicted in reasonable agreement with experiment. Such predictions cannot approach the precision of two decimal places or better required to map the locus of phase matching for second-harmonic generation in a crystal. They can however interpret existing measurements and supplement them where they are incomplete, for example because of problems with crystal growth or habit. One recent example is the prediction of the missing refractive index in the α-sexithiophene crystal, which proves to be large [45].

Acknowledgments

This paper is respectfully dedicated to the memory of the late Professor Krzysztof Pigoń, in recognition of his foresight in helping to establish the flourishing activity in molecular materials at the Technical University of Wrocław. The authors' collaboration was fostered by EU TMR Network Grant FMRX-CT96-0047 and by a European Science Exchange Programme grant from the Royal Society.

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