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To cite this article: Jérémy R Rouxel *et al* 2018 *J. Phys. B: At. Mol. Opt. Phys.* **51** 034004

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# Translational and rotational averaging of nonlocal response tensors for nano-shaped light

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Received 4 August 2017, revised 6 November 2017

Accepted for publication 27 November 2017

Published 16 January 2018



## Abstract

Oriental averaging of response tensors is an essential operation in calculating optical signals in randomly oriented liquid or gas phase molecular ensembles. When expanded in multipoles, rotational averaging can be performed simply through contraction with isotropic tensors. Alternatively, the multipolar expansion can be avoided and all multipoles may be naturally and implicitly incorporated via nonlocal response tensors which are fields and may not be rotationally averaged in a simple manner. The nonlocal response is useful when the light beam variation across the system is non negligible. Examples are nano-sculpted or short wavelength x-ray field. We derive exact expressions which recast optical signals as a convolution of a nonlocal response function of matter with a nonlocal intrinsic property of the electromagnetic field. The approach involves a gauge invariant calculation based on the minimal coupling Hamiltonian.

Keywords: chirality, nonlocal response, orientational averaging, gas phase spectroscopy, chemical physics

(Some figures may appear in colour only in the online journal)

Experimental and engineering advances in the development of new electromagnetic sources [1, 2] and nanofabrication [3] make it possible to explore novel light–matter interaction regimes. Part of the fascinating properties of nanosystems is that their size is comparable or smaller than the wavelength in the visible spectrum. To describe their interaction with light, it is necessary to take into account the nonlocal nature of the response [4]. This can be done by including higher multipoles. The drawback is that high order multipoles are not simple to understand physically. By alternatively describing the interaction in terms of current and charge densities allows to take in account the nonlocality while using physically intuitive quantities. Previously, we applied the nonlocal responses of a single particle to study chiral [5] or x-ray [6]

signals. However, to describe the signals from molecules in solution, one has to consider rotationally and translationally averaged nonlocal response functions. The averaging protocol of local response tensors is well developed [7–9] but the nonlocal case is more involved mathematically [10, 11] since it deals with tensor field and has not been considered so far. Such averaging of nonlocal response tensor becomes increasingly important with the development of nano-sculpted fields.

Here we formulate the optical response using the minimal coupling Hamiltonian and derive exact general expressions for the nonlocal response of a randomly oriented sample. By working with the nonlocal response rather than multipoles we avoid the tedious canonical transformation to the multipolar Hamiltonian. Our results define precisely the joint field+matter quantity to be optimized. We show how to translationally and

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orientationally average the nonlocal response tensors by using a projection over invariant subsets instead of doing an ensemble average. Besides nanostructures, the present formalism may be used for spectroscopy with short wavelength (e.g x-ray) fields and to the study of chirality.

## 1. The nonlocal response functions

We start by reviewing the nonlocal response functions for heterodyne resonant linear signals (useful for chiral sensing and nanoptics) and for spontaneous x-ray diffraction signals. The minimal coupling Hamiltonian for the radiation/matter coupling is

$$H_{\text{int}}(t) = -\int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, t) + \frac{e}{2mc} \int d\mathbf{r} \sigma(\mathbf{r}) A^2(\mathbf{r}, t), \quad (1)$$

where  $\mathbf{A}$  is the vector potential of the electromagnetic field,  $e$  and  $m$  are the electron charge and mass and  $c$  is the speed of light. Charge and current are simple operators as opposed to multipoles.

$$\sigma(\mathbf{r}) = e\psi^\dagger(\mathbf{r})\psi(\mathbf{r}) \quad (2)$$

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi}(\psi^\dagger(\mathbf{r})\nabla\psi(\mathbf{r}) - (\nabla\psi(\mathbf{r})^\dagger)\psi(\mathbf{r})). \quad (3)$$

Here,  $\psi^\dagger(\mathbf{r})$  and  $\psi(\mathbf{r})$  are the electron field Fermion creation and annihilation operators at position  $\mathbf{r}$ .  $\mathbf{j}(\mathbf{r})$  is a purely material current density operator and is gauge non-invariant [12]. Using this Hamiltonian, we can express optical signals as correlation functions of charge and current densities of matter [12]. The response functions are nonlocal in space and time. Signals simulated in the multipolar approach, truncated at a given multipolar order, are in that sense an approximation of those calculated in the minimal coupling picture.

Generally, the nonlocal linear response tensor is given by a multipoint correlation of the current densities for resonant interactions. At the lowest order, i.e. for linear resonant spectroscopy, it is a two-point correlation function of the current density  $\zeta(\mathbf{r}, \mathbf{r}_1, t_1)$  which can be expressed as

$$\zeta(\mathbf{r}, \mathbf{r}_1, t_1) = \langle \Psi(t_0) | \mathbf{j}(\mathbf{r}) G(t_1) \mathbf{j}(\mathbf{r}_1) | \Psi(t_0) \rangle, \quad (4)$$

where  $|\Psi(t_0)\rangle$  is the initial state of the system before interaction and  $G(t_1)$  is the non-perturbed molecular propagator. The  $\sigma$  term gives a small off-resonant correction. The corresponding linear signal is obtained through an integration with the incoming field

$$S^{(1)} = \int d\mathbf{r} d\mathbf{r}_1 dt dt_1 \zeta(\mathbf{r}, \mathbf{r}_1, t_1) \mathbf{A}(\mathbf{r}, t) \mathbf{A}(\mathbf{r}_1, t - t_1), \quad (5)$$

where we have omitted the variable on which depends  $S^{(1)}$ . There variables are usually the central frequency of the  $\mathbf{A}$  field, its FWHM and its polarization. In the nonlocal picture, the signal will also depend on the spatial parameters of the incoming beam that can also be varied and scanned.

## 2. Rotational and translation averaging of response functions

In this section, we consider various averaging schemes. Details are given in appendices A–C. In these appendices, the components of the matter quantities (current or charge density transition matrix elements) are expanded over a basis of Cartesian Gaussian type orbitals (GTO). In many cases such as in gas or liquids, a randomly oriented sample possesses also translational invariance. Only rotational averaging is required in the case of a molecule in a spherical trap for example.

We shall omit the time dependence of the nonlocal response tensor for brevity. Additionally, one can consider a non uniform probability density that would physically correspond to a non-homogeneous distribution of the molecule in space. However, as shown in appendix A, this is equivalent to considering nonlocal exciting fields and we will follow that path instead. The translational averaging is given by

$$\langle \zeta \rangle_T(\mathbf{r}, \mathbf{r}_1) = \int_{\mathbb{R}^3} \zeta(\mathbf{r} + \tilde{\mathbf{r}}, \mathbf{r}_1 + \tilde{\mathbf{r}}) d\tilde{\mathbf{r}}. \quad (6)$$

Making the change of variables  $\tilde{\mathbf{r}} \rightarrow \tilde{\mathbf{r}} - \mathbf{r}_1$  and defining  $\mathbf{R} = \mathbf{r} - \mathbf{r}_1$ , we get:

$$\langle \zeta \rangle_T(\mathbf{R}) = \int_{\mathbb{R}^3} \zeta(\mathbf{R} + \tilde{\mathbf{r}}, \tilde{\mathbf{r}}) d\tilde{\mathbf{r}}. \quad (7)$$

The integral is carried out in appendix A for current densities expanded over a Cartesian GTO basis. The components of the response tensor are then expressed as a sum of Cartesian GTO.

We now turn to rotational averaging of the response tensor. For a translationally invariant system, the linear response depends only on the  $\mathbf{R}$  variable. The rotational averaging of a tensor field over a three dimensional space is given by:

$$\langle \zeta \rangle_{T,\Omega}(\mathbf{R}) = \int_{\omega} \hat{R}_{\omega} \langle \zeta \rangle_T(\hat{R}_{\omega}^{-1} \mathbf{R}) d\alpha \sin \beta d\beta d\gamma, \quad (8)$$

where  $\langle \dots \rangle_{\Omega}$  stands for the rotational averaging, and  $\hat{R}_{\omega}$  is the rotation operator expressed in terms of Euler angles  $\omega = (\alpha, \beta, \gamma)$ . The rotation operator reduces to the usual rotation matrix when applied on  $\mathbf{R}$  and to Wigner  $\mathcal{D}$  matrices when applied on an irreducible tensor. However, this averaging protocol is difficult to implement in practice and one should use some symmetry arguments to simplify it.

A rotationally invariant response function can be generally obtained using representation theory in the following way. The response function  $\langle \zeta \rangle_T(\mathbf{R})$  is a second rank tensor that corresponds to the coupling of two  $J=1$  angular momenta. The coupling of angular momenta [13] leads to total angular momenta  $J=0, 1, 2$ . The  $J=0$  irreducible component of the tensor is its rotationally invariant part. It can be obtained by projecting the response on the  $J=0$  tensor spherical harmonics of the same rank. The rotationally averaged response tensor can be expanded as a sum of tensor spherical harmonics  $\mathbf{Y}_{ls}^{JM}$  with zero total angular momentum  $J$  (see appendix D):

$$\langle \zeta \rangle_{T,\Omega}(\mathbf{R}) = \sum_{s=0}^2 \zeta_{ss}^{00}(\mathbf{R}) \mathbf{Y}_{ss}^{00}(\theta, \varphi), \quad (9)$$

where we have used  $l = s$  (because  $|l - s| \leq 0$ ). The coefficients  $\zeta_{ss}^{00}(R)$  of this expansion are defined by:

$$\zeta_{ss}^{00}(R) = \int_{\Omega} \langle \zeta \rangle_{T,\Omega}(R) \cdot \mathbf{Y}_{ss}^{00}(\theta, \varphi) d\Omega, \quad (10)$$

where  $\Omega$  is the solid angle. Now, one can average the non-rotationally invariant  $\langle \zeta \rangle_T(\mathbf{R})$  tensor by projecting it over the subset of its rotationally invariant components. Our final expression for calculating the rotational average of the  $\langle \zeta \rangle_T(\mathbf{R})$  is then

$$\langle \zeta \rangle_{T,\Omega}(R) = \sum_s \left( \int_{\Omega} \langle \zeta \rangle_T(\mathbf{R}) \cdot \mathbf{Y}_{ss}^{00}(\theta', \varphi') d\Omega' \right) \mathbf{Y}_{ss}^{00}(\theta, \varphi). \quad (11)$$

This definition makes the rotational averaging numerically tractable by replacing the averaging over ensemble by a projection. It is calculated in appendix C for a response tensor expanded over spherical GTO. We emphasize that the rotationally and translationally averaged nonlocal response function is expanded over only three isotropic components, equation (9). Only the  $s = 1$  term contributes to chiral signal and it is the overlap with that term and the corresponding field component that needs to be maximized to increase the magnitude of chiral signals. The conversion from the Cartesian GTO to the spherical GTO is given in appendix B. Projecting both the matter response function and the nonlocal exciting fields, we can express the averaged linear signal as a sum over the  $J = 0$  irreducible tensors:

$$S^{(1)} = \sum_s \int d\mathbf{R} d\tilde{\mathbf{r}} \zeta_{ss}^{J=0}(R) \cdot \mathbf{F}_s^{J=0}(\mathbf{R}, \tilde{\mathbf{r}}), \quad (12)$$

where  $R$  is the norm of  $\mathbf{R}$ . The  $F$  tensor describes the various irreducible components of the vector potential direct products that have a total angular momentum  $J = 0$ , i.e. interacts with the rotationally invariant part of the response tensor. The matter response can be factorized out of the integral over  $\tilde{\mathbf{r}}$  and the angular part of the integral over  $\mathbf{R}$ , leading to

$$S^{(1)} = \sum_s \int dR \zeta_{ss}^{J=0}(R) \cdot \mathcal{F}_s(R), \quad (13)$$

where the distance-dependent bilinear functionals of the field  $\mathcal{F}(R)$  have the form

$$\mathcal{F}_s(R) = \int d\tilde{\mathbf{r}} \int_{S^2} d\mathbf{n} F_s(\mathbf{R}, \tilde{\mathbf{r}}) \quad (14)$$

with  $\mathbf{n}$  is the unit vector in the direction of  $\mathbf{R}$  and

$$\begin{aligned} F_0 &= \frac{1}{\sqrt{3}} (\mathbf{A}(\tilde{\mathbf{r}}) \cdot \mathbf{A}(\tilde{\mathbf{r}} + R\mathbf{n})), \\ F_1 &= \frac{1}{\sqrt{2}} (\mathbf{A}(\tilde{\mathbf{r}}) \times \mathbf{A}(\tilde{\mathbf{r}} + R\mathbf{n})) \cdot \mathbf{n}, \\ F_2 &= \frac{\sqrt{6}}{2} (\mathbf{n} \cdot \mathbf{A}(\tilde{\mathbf{r}})) (\mathbf{n} \cdot \mathbf{A}(\tilde{\mathbf{r}} + R\mathbf{n})) - \frac{1}{\sqrt{3}} F_0. \end{aligned} \quad (15)$$

It is possible to write these functionals in component notation  $F_s = \sum_{ij} F_s^{ij} A_i(\tilde{\mathbf{r}}) A_j(\tilde{\mathbf{r}} + R\mathbf{n})$  where the  $F_s^{ij}$  are defined by

$$F_0^{ij} = \frac{\delta^{ij}}{\sqrt{3}}, \quad (16)$$

$$F_1^{ij} = \frac{1}{\sqrt{2}} n^k \epsilon_k^{ij}, \quad (17)$$

$$F_2^{ij} = \frac{\sqrt{6}}{2} n^i n^j - \frac{\delta^{ij}}{3}. \quad (18)$$

Equations (13)–(15) point out to which field quantity should be optimized in order to maximize the overlap with the matter response and hence the signal. The  $\mathcal{F}_1(R)$  component provides a unique measure of field chirality and expresses the chiral linear response of a molecule which lacks an inversion center in terms of  $\mathcal{F}_1(R)$  and the response function  $\zeta_1^{J=0}(R)$  as a one-dimensional overlap integral over  $R$ . Note that in the long-wave limit the nonlocal functional  $\mathcal{F}_1(R)$  becomes local. A simple long-wave limit expansion substituted into equation (15), reproduces the universal functional [14]

$$S^{(1)} = \frac{1}{3\sqrt{2}} \int_0^\infty dR R^3 \zeta_1(R) \times \int d\mathbf{R} \mathbf{A}^*(\mathbf{R}) \cdot \text{rot} \mathbf{A}(\mathbf{R}). \quad (19)$$

### 3. Rotational but not translational averaging of the response functions

When only rotational averaging is needed. The rotation average response function is defined by

$$\langle \zeta \rangle_{\Omega}(r, r_1, \theta) = \int_{\omega} \hat{R}_{\omega} \zeta(\hat{R}_{\omega}^{-1} \mathbf{r}, \hat{R}_{\omega}^{-1} \mathbf{r}_1) d\alpha \sin \beta d\beta d\gamma. \quad (20)$$

This corresponds to a single molecule in a spherically symmetric trap. In this case, one has to average the 6 dimensional tensor field  $\zeta(\mathbf{r}, \mathbf{r}_1)$ . Similarly to the rotationally and translationally averaged linear response, it is possible to achieve the averaging by projection over an appropriate nonlocal isotropic basis. We use spherical harmonics but the presence of two arguments  $\mathbf{r}$  and  $\mathbf{r}_1$  requires then to use the more cumbersome bipolar spherical harmonics [13]. Instead, we introduce a different approach to define the rotation invariant tensor basis. After rotational averaging, the norms of the  $\mathbf{r}_1$  and  $\mathbf{r}_2$  vectors and their relative angle  $\theta$  is sufficient to describe a specific configuration. This is equivalent to the description of triatomic molecules in terms of bond lengths and internal angle. In the same way, translational–rotational averaging only involves a single variable  $R$  similarly to the description of diatomic molecules. The signal  $S_{\text{stim}}$  can be represented as a sum of nine functionals:

$$S^{(1)} = \sum_{las} \int dr dr_1 d\theta \zeta_{las}(r, r_1, \theta) \cdot F_{las}(r, r_1, \theta), \quad (21)$$

where  $\zeta_{las}(r, r_1, \theta)$  and  $F_{las}(r, r_1, \theta)$  are the projection onto the invariant basis of the matter correlation function and the field tensor, respectively. The ‘ $\cdot$ ’ represents the scalar product in the invariant basis and we introduce it in the following. The nine invariants basis functionals  $G_{las}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1))$  are

given by

$$\begin{aligned}
G_{000}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= \mathbf{X}(\mathbf{r}) \cdot \mathbf{Y}(\mathbf{r}_1) \\
G_{100}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= (\mathbf{r} \times \mathbf{r}_1) \cdot (\mathbf{X}(\mathbf{r}) \times \mathbf{Y}(\mathbf{r}_1)) \\
G_{11s}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= \mathbf{r}_s \cdot (\mathbf{X}(\mathbf{r}) \times \mathbf{Y}(\mathbf{r}_1)) \\
G_{20s}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= (\mathbf{r}_s \cdot \mathbf{X}(\mathbf{r}))(\mathbf{r}_s \cdot \mathbf{Y}(\mathbf{r}_1)) \\
&\quad - \frac{1}{3} r_s^2 \mathbf{X}(\mathbf{r}) \cdot \mathbf{Y}(\mathbf{r}_1), \\
G_{200}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= (\mathbf{r}_s \cdot \mathbf{X}(\mathbf{r}))(\mathbf{r} \times \mathbf{r}_1) \cdot \mathbf{Y}(\mathbf{r}_1) \\
&\quad + (\mathbf{r}_s \cdot \mathbf{Y}(\mathbf{r}_1))(\mathbf{r} \times \mathbf{r}_1) \cdot \mathbf{X}(\mathbf{r}), \\
G_{21s}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) &= (\mathbf{r} \cdot \mathbf{X}(\mathbf{r}))(\mathbf{r}_1 \cdot \mathbf{Y}(\mathbf{r}_1)) \\
&\quad + (\mathbf{r}_1 \cdot \mathbf{X}(\mathbf{r}))(\mathbf{r} \cdot \mathbf{Y}(\mathbf{r}_1)) \\
&\quad - \frac{2}{3} (\mathbf{r} \cdot \mathbf{r}_1)(\mathbf{X}(\mathbf{r}) \cdot \mathbf{Y}(\mathbf{r}_1)), \quad (22)
\end{aligned}$$

where  $s = 1, 2$ . We can interpret  $G_{las}^{kl}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1))$  as rotation invariant tensor functions of  $(\mathbf{r}, \mathbf{r}_1)$  by representing the local functionals  $G_{las}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1))$  as

$$G_{las}(\mathbf{X}(\mathbf{r}), \mathbf{Y}(\mathbf{r}_1)) = \sum_{ij} G_{las}^{ij}(\mathbf{r}, \mathbf{r}_1) \mathbf{X}_i(\mathbf{r}) \mathbf{Y}_j(\mathbf{r}_1). \quad (23)$$

$G_{las}^{ij}$  form a basis set in the space of rotational invariant rank 2 tensor functions of  $(\mathbf{r}, \mathbf{r}_1)$ . Using the summation of repeated indices convention, this basis is explicitly written as

$$\begin{aligned}
G_{000}^{ij}(\mathbf{r}, \mathbf{r}_1) &= \delta^{ij} \\
G_{100}^{ij}(\mathbf{r}, \mathbf{r}_1) &= \epsilon_{kl}^m r^k r_1^l \delta_m^n \epsilon_n^{ij} \\
G_{11s}^{ij}(\mathbf{r}, \mathbf{r}_1) &= r_s^n \cdot \epsilon_n^{ij} \\
G_{20s}^{ij}(\mathbf{r}, \mathbf{r}_1) &= r_s^i r_s^j - \frac{1}{3} r_s^2 \delta^{ij} \\
G_{200}^{ij}(\mathbf{r}, \mathbf{r}_1) &= r_s^i \epsilon_{mn}^j r^m r_1^n + r_s^j \epsilon_{mn}^i r^m r_1^n \\
G_{21s}^{ij}(\mathbf{r}, \mathbf{r}_1) &= r^i r_1^j + r_1^i r^j - \frac{2}{3} r_m r_1^m \delta^{ij}, \quad (24)
\end{aligned}$$

where  $\epsilon$  is the Levi-Civita symbol. We can then expand both the matter correlation function and the field tensor over this basis

$$\zeta_{ij}(\mathbf{r}, \mathbf{r}_1; \omega) = \sum_{las} \zeta(r, r_1, \theta; \omega) G_{las}^{ij}(\mathbf{r}, \mathbf{r}_1), \quad (25)$$

$$F_{ij}(\mathbf{r}, \mathbf{r}_1; \omega) = \sum_{las} (\mathbf{A} \otimes \mathbf{A})(r, r_1, \theta; \omega) G_{las}^{ij}(\mathbf{r}, \mathbf{r}_1), \quad (26)$$

Their scalar product is defined by

$$m_{la,ss'}(\mathbf{r}, \mathbf{r}_1) = \text{Tr}(G_{las}^\dagger(\mathbf{r}, \mathbf{r}_1) G_{las'}(\mathbf{r}, \mathbf{r}_1)). \quad (27)$$

They are readily evaluated

$$\begin{aligned}
m_{00,00} &= 3, \\
m_{10,00} &= r^2 r_1^2 \sin^2 \theta, \\
m_{11,ss'} &= \mathbf{r}_s \cdot \mathbf{r}_{s'}, \\
m_{20,00} &= 2r^2 r_1^2 + \frac{2}{3} (\mathbf{r} \cdot \mathbf{r}_1)^2, \\
m_{20,0s} &= 2(\mathbf{r} \cdot \mathbf{r}_s)(\mathbf{r}_1 \cdot \mathbf{r}_s) - \frac{2}{3} (\mathbf{r} \cdot \mathbf{r}_1) r_s^2, \\
m_{20,ss'} &= (\mathbf{r}_s \cdot \mathbf{r}_{s'})^2 - \frac{1}{3} r_s^2 r_{s'}^2, \\
m_{21,ss'} &= 2(\mathbf{r}_s \cdot \mathbf{r}_{s'}) r^2 r_1^2 \sin^2 \theta. \quad (28)
\end{aligned}$$

The stimulated signal can then be recast as

$$S^{(1)} = \sum_{lass'} \int dr dr_1 d\theta m_{la}^{ss'} \zeta_{las'}(r, r_1, \theta) F_{las}(r, r_1, \theta), \quad (29)$$

where  $m_{la}^{ss'}$  is the inverse matrix of the scalar products of invariant tensor functions obtained from the condition

$$\sum_r m_{la}^{sr}(r, r_1, \theta) m_{la,rs'}(r, r_1, \theta) = \delta_{ss'}. \quad (30)$$

Equation (29) is equivalent to equation (21) with the scalar product explicitly given in terms of the  $m_{la,ss'}$ . In the above expressions the index  $a$  denotes even ( $a=0$ ) and odd ( $a=1$ ) parity.

Out of the 9 contributions to the linear response in a spherically symmetric trap, 4 terms are chiral ( $a=1$ ) and 5 non-chiral ( $a=0$ ). All  $a=1$  components of  $\zeta_{las}$  vanish for non-chiral molecules. It is easy to see that if the fields  $\mathbf{A}_{\text{het}}(\mathbf{r})$  and  $\mathbf{A}(\mathbf{r}_1)$  have a well-defined and opposite parity with respect to inversion via the spherical symmetry center of the trap, we have  $F_{las} = 0$  when  $a=0$ . Therefore, in such setting the linear response of non-chiral molecules vanishes and appropriate spatial tuning of the incoming fields can provide a background-free measurement of molecular chirality.

#### 4. Other applications; chiral signals and x-ray diffraction

An important effort has been made towards the optimization of chiral signals using ultrafocussed or spatially varying light at the molecular scale. The nonlocal response may be used for these applications. Chiral molecules that lack inversion symmetry play important roles in biological activity. Chiral signals such as circular dichroism (CD) or optical rotatory dispersion [15] are intrinsically weak (typically order  $ka$  smaller than non-chiral signals, where  $k$  and  $a$  are the light wavevector and molecular size) compared to their non-chiral counterparts, typically by a factor  $10^{-2}$ – $10^{-3}$  in the visible regime. Enhancing the chiral response has been a long-standing goal of many applications such as to chemical sensors. Cohen and co-workers [16] have discussed ways of enhancing chiral signals by manipulating nano-optical fields to have strong spatial variation. Such manipulations of the field are now possible by nano-antennas [17]. Within the magnetic dipole approximation [18], they have identified an intrinsic property of the electromagnetic field, the field chirality [19], that is responsible for chiral signals and then discussed how to maximize the field chirality using spatially sculpted fields [20]. Adding the magnetic dipole in the interaction expansion amounts to taking into account small variations of the electromagnetic fields across the molecule. When the field variation becomes more pronounced and the structure is larger, additional multipoles must be included. A discussion in term of nonlocal quantities (charge and current densities) can shed a new light on the physical nature of the chiral response.

The resonant response is dominated by the first (current) coupling in equation 1. The stimulated (heterodyne), linear



CD signal is then given by [5]

$$S_{\text{CD}}^{(1)} = \text{Im} \int d\mathbf{r} d\mathbf{r}_1 dt_1 \langle \zeta(\mathbf{r}, \mathbf{r}_1, t_1) \rangle_{T, \Omega} \\ \times (\mathbf{A}_{\text{het}}^+(\mathbf{r}, t) \mathbf{A}^+(\mathbf{r}_1, t - t_1) - \mathbf{A}_{\text{het}}^-(\mathbf{r}, t) \mathbf{A}^-(\mathbf{r}_1, t - t_1)), \quad (31)$$

where  $\mathbf{A}_{\text{het}}(\mathbf{r}_2, t)$  is the heterodyne (local oscillator) field and  $\mathbf{A}(\mathbf{r}_1, t - t_1)$  is the driving field. For standard local CD, the fields are plane waves of wavelength much larger than the molecule size, allowing for a quickly converging multipolar expansion, and the difference of the linear absorption is taken between left polarized (noted +) and right polarized (noted -). In the nonlocal extension, the fields in the signals are replaced by beams spatially varying across the molecule and carrying an orbital angular momentum, such as Laguerre–Gauss beams.

In other developments, new light sources such as x-ray free electron laser [21] or high harmonic generation [22] allow to carry out coherent nonlinear spectroscopies in the x-ray regime. While much can be learned from the IR, visible and UV experiments, a large number of multipoles may become relevant in the interaction due to the short wavelength of x-ray light. It is then customary to use instead the minimal coupling Hamiltonian that circumvents the multipolar expansion and uses the more intuitive charge and current densities instead. Moreover, scattering processes involved in diffraction signals are usually expressed using the  $\sigma \mathbf{A}^2$  term in the minimal coupling Hamiltonian [23]. Gas phase phase diffraction are dominated by one-molecule contribution and their matter correlation function is thus a two-point correlation function of the charge density. The averaging techniques presented here focus on the correlation function involving the current densities but they can readily be applied to multipoint correlation functions of the charge density (or mixed current/charge ones).

We consider for example spontaneous off-resonant x-ray diffraction signals. X-ray diffraction is usually carried out in crystals to preserve long-range order. In that case, the signal is dominated by two-molecule contributions [24]. In randomly oriented samples, the signal is given by the one-molecule contribution [25] which is given by

$$S^{\text{diff}} \propto \int d\mathbf{r} d\mathbf{r}' dt dt' e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \\ \times \langle \sigma(\mathbf{r}, t) \sigma(\mathbf{r}', t') \rangle_{T, \Omega} \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{A}(\mathbf{r}', t'), \quad (32)$$

where  $\langle \dots \rangle$  stands for the expectation value of the operator within the brackets. The matter correlation function  $\langle \sigma(\mathbf{r}, t) \sigma(\mathbf{r}', t') \rangle$  is also a two-point correlation function in space as in the nonlocal signal in equation (31) and averaging techniques presented in this paper can be applied to it as well. The  $\langle \sigma \sigma \rangle$  correlation function is a scalar field and is then much simpler to average using scalar bipolar spherical harmonics.

## 5. Conclusions

In this paper, we have addressed a broad class of signals that can be recast in terms of nonlocal response functions. Nonlocality becomes increasingly important for strongly varying electromagnetic fields over the relevant region of space. We have provided techniques for averaging these nonlocal response tensor in rotationally and translationally invariant systems, e.g. liquids and gases. We then showed how the signal is finally given by the spatial overlap integral between the average matter response tensor and a nonlocal field tensor. This permits the calculation of spectroscopic signal of e.g. colloidal solutions of nanoparticles or x-ray diffraction in gas or liquid phase.

We have treated ensemble averaging over multiple molecules within the exciting pulse excitation volume. Another possibility is to use a small excitation volume in which molecules pass through randomly during the detection time. Thus, one needs to consider a time average of molecular orientations within the excitation volume and, using the ergodic principle, this average can be done with the averaging discussed here.

The averaging technique presented here can be used to simulate such signals and it also provides a guideline for amplifying intrinsically weak chiral signals. We have shown previously that the intrinsic relevant chirality of the electromagnetic field is a nonlocal property which, when convoluted with the nonlocal matter response, gives the chiral signal [5]. Thus, the optimization of the chiral response using nano-shaped light must depend on the nature of the nonlocal molecular response. In particular, we have shown that chiral signals originate from a subset of the  $J = 0$  irreducible components of the field tensor. To enhance these chiral signals, one must then focus on maximizing the spatial overlap between this component of the fields and the corresponding chiral irreducible part of the response tensor. Unlike the magnetic dipole approximation where the chiral signals are related to a universal local chirality of the field [16], more generally, we need to optimize the field taking into account the form of the nonlocal matter response. Then, the best field chirality has to be defined with respect to the chiral part of the molecular response tensor and is not simply a number as described in the dipole (local) approximation. The field chirality is then a nonlocal property of the electromagnetic field. In the nonlocal translationally and rotationally averaged case, it is a function of one argument and in the rotationally only averaged case, it is four functions of three arguments. Specific molecular traps will create different averaging geometries and the nonlocal field chirality changes accordingly. Another route to explore chirality using nonlocal response tensors has made use of beams carrying an orbital angular momentum such as Laguerre–Gauss beams [26]. These are widely unexplored possibilities to enhance nonlocal signals using spatially shaped pulses.

## Acknowledgments

The support of the National Science Foundation (Grant No CHE-1663822) and of the Chemical Sciences, Geosciences, and Biosciences division, Office of Basic Energy Sciences, Office of Science, US Department of Energy through Award No. DE-FG02-04ER15571 is gratefully acknowledged. JR was supported by the DOE grant.

## Appendix A. Translational averaging of GTOs

The components of the response tensor can be written as a direct product of current densities. Omitting the time variables that do not need to be integrated over space [5, 12], we have

$$\begin{aligned} \int_{\mathbb{R}^3} \zeta_{ij}(\mathbf{R} + \tilde{\mathbf{r}}, \tilde{\mathbf{r}}, t_1) d\tilde{\mathbf{r}} &= \int_{\mathbb{R}^3} \langle j_i(\mathbf{R} + \tilde{\mathbf{r}}, t_1) j_j(\tilde{\mathbf{r}}, t_0) \rangle d\tilde{\mathbf{r}} \\ &\rightarrow \int_{\mathbb{R}^3} j_i(\mathbf{R} + \tilde{\mathbf{r}}) j_j(\tilde{\mathbf{r}}) d\tilde{\mathbf{r}}. \end{aligned} \quad (33)$$

The components of the current density are expanded over Cartesian GTO:

$$j_i(\mathbf{r}) = \sum_n c_{in} g_c(k_n, l_n, m_n, r_n, \alpha_n), \quad (34)$$

$$\begin{aligned} g_c(k_n, l_n, m_n, r_n, \alpha_n) &= (x - x_n)^{k_n} (y - y_n)^{l_n} \\ &\times (z - z_n)^{m_n} e^{-\alpha_n(\mathbf{r} - \mathbf{r}_n)^2}. \end{aligned} \quad (35)$$

The integral over the product of current densities can be calculated:

$$\begin{aligned} \int_{\mathbb{R}^3} j_i(\mathbf{R} + \tilde{\mathbf{r}}) j_j(\tilde{\mathbf{r}}) d\tilde{\mathbf{r}} &= \sum_{mn} c_{jm} c_{in} \\ &\times \int_{\mathbb{R}^3} g_c(k_n, l_n, m_n, r_n - r, \alpha_n) g_c(k_m, l_m, m_m, r_m, \alpha_m) \\ &= \sum_{mn} c_{jm} c_{in} e^{-\frac{\alpha_n \alpha_m}{\alpha_n + \alpha_m} (\mathbf{r} - (\mathbf{r}_n - \mathbf{r}_m))^2} S_x S_y S_z, \end{aligned} \quad (36)$$

$$\begin{aligned} S_x &= \sqrt{\frac{\pi}{\alpha}} \sum_{i_x=0}^{k_n} \sum_{j_x=0}^{k_m} \binom{k_n}{i_x} \binom{k_m}{j_x} \frac{(k_m + k_n - 1)!!}{(2\alpha)^{\frac{i_x + j_x}{2}}} \\ &\times (x_p - x_n + x)^{k_n - i_x} (x_p - x_m)^{k_m - j_x}, \end{aligned} \quad (37)$$

$$\begin{aligned} S_y &= \sqrt{\frac{\pi}{\alpha}} \sum_{i_y=0}^{l_n} \sum_{j_y=0}^{l_m} \binom{l_n}{i_y} \binom{l_m}{j_y} \frac{(l_m + l_n - 1)!!}{(2\alpha)^{\frac{i_y + j_y}{2}}} \\ &\times (y_p - y_n + y)^{l_n - i_y} (y_p - y_m)^{l_m - j_y}, \end{aligned} \quad (38)$$

$$\begin{aligned} S_z &= \sqrt{\frac{\pi}{\alpha}} \sum_{i_z=0}^{m_n} \sum_{j_z=0}^{m_m} \binom{m_n}{i_z} \binom{m_m}{j_z} \frac{(m_m + m_n - 1)!!}{(2\alpha)^{\frac{i_z + j_z}{2}}} \\ &\times (z_p - z_n + z)^{m_n - i_z} (z_p - z_m)^{m_m - j_z}, \end{aligned} \quad (39)$$

$$\alpha = \alpha_m + \alpha_n, \quad (40)$$

$$\mathbf{r}_p = \frac{\alpha_n(\mathbf{r}_n - \mathbf{r}) + \alpha_m \mathbf{r}_m}{\alpha}. \quad (41)$$

The integration has been calculated analytically but it is not in the form of a sum of Cartesian GTO depending on  $\mathbf{r}$ . Defining  $\Delta \mathbf{r} = \mathbf{r}_n - \mathbf{r}_m$ , this can be achieved by simplifying the following product of monomials:

$$\begin{aligned} &(x_p - x_n + x)^{k_n - i_x} (x_p - x_m)^{k_m - j_x} \\ &= \left( \frac{\alpha_m}{\alpha} \right)^{k_n - i_x} (x - (x_n + x_m))^{k_n - i_x} \left( -\frac{\alpha_n}{\alpha} \right)^{k_m - j_x} \\ &\times (x + (x_n + x_m))^{k_m - j_x} \\ &= \left( \frac{\alpha_m}{\alpha} \right)^{k_n - i_x} (x - \Delta x - 2x_m)^{k_n - i_x} \left( -\frac{\alpha_n}{\alpha} \right)^{k_m - j_x} \\ &\times (x - \Delta x + 2x_n)^{k_m - j_x}. \end{aligned} \quad (42)$$

Using the binomial expansion, we get:

$$\begin{aligned} (x - \Delta x - 2x_m)^{k_n - i_x} &= \sum_{k_1=0}^{k_n - i_x} \binom{k_n - i_x}{k_1} \\ &\times (x - \Delta x)^{k_n - i_x - k_1} (-2x_m)^{k_1}. \end{aligned} \quad (43)$$

Using the same steps for the products of monomials in  $S_y$  and  $S_z$ , we finally obtain the result of the initial integral as a sum of Cartesian GTO:

$$\begin{aligned} \int_{\mathbb{R}^3} j_i(\mathbf{R} + \tilde{\mathbf{r}}) j_j(\tilde{\mathbf{r}}) d\tilde{\mathbf{r}} &= \sum_{mn} c_{in} c_{jm} \left( \frac{\pi}{\alpha} \right)^{\frac{3}{2}} \\ &\times \sum_{i_x, j_x, k_1, k_2} \sum_{i_y, j_y, l_1, l_2} \sum_{i_z, j_z, m_1, m_2} A_{i_x j_x}^{k_1 k_2} A_{i_y j_y}^{l_1 l_2} A_{i_z j_z}^{m_1 m_2} \\ &g_c(k_n + k_m - i_x - j_x - k_1 - k_2, \dots, \Delta \mathbf{r}, \frac{\alpha_n \alpha_m}{\alpha_n + \alpha_m}), \end{aligned} \quad (44)$$

$$\begin{aligned} A_{i_x j_x}^{k_1 k_2} &= \binom{k_n}{i_x} \binom{k_m}{j_x} \binom{k_n - i_x}{k_1} \binom{k_m - j_x}{k_2} \frac{(k_m + k_n - 1)!!}{(2\alpha)^{\frac{i_x + j_x}{2}}} \\ &\times \left( \frac{\alpha_m}{\alpha} \right)^{k_n - i_x} \left( -\frac{\alpha_n}{\alpha} \right)^{k_m - j_x} (-2x_m)^{k_1} (2x_n)^{k_2}. \end{aligned} \quad (45)$$

With similar expressions for  $A_{i_y j_y}^{l_1 l_2}$  and  $A_{i_z j_z}^{m_1 m_2}$ .

## Appendix B. Conversion of Cartesian GTO to spherical GTO

We consider that the components of the response tensor have been rotationally averaged and, using the results of the previous appendix, expressed as a sum of Cartesian GTO. The rotational averaging is easier to accomplished using spherical GTO and we review in this section how to do this change of basis. The coefficients of the transformation have been calculated by Schlegel and Frisch [27] and we simply state their results here. Unnormalized spherical GTO are defined as:

$$g_s(l, m, n, \mathbf{r}', \alpha) = r^n e^{-\alpha(\mathbf{r} - \mathbf{r}')^2} Y_{lm}(\theta, \varphi). \quad (46)$$

The spherical GTO are constructed from the Cartesian GTO in the following way:

$$\begin{aligned} r^{l-n} g_s(l, m, n, \mathbf{r}, \alpha) &= \sum_{l_x + l_y + l_z = l} c(l, m, n, l_x, l_y, l_z) g_c(l_x, l_y, l_z, \mathbf{r}, \alpha), \end{aligned} \quad (47)$$

$$c(l, m, n, l_x, l_y, l_z) = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} \frac{1}{l_x!l_y!l_z!} \\ \times \left( \frac{d^l}{dx^{l_x} dy^{l_y} dz^{l_z}} (x \pm iy)^{|m|} \frac{1}{2^l l!} \frac{\partial^{l+|m|}}{\partial z^{l-|m|}} \right) \\ \times (z^2 - r^2)^l \Big|_{x=0, y=0, z=0}. \quad (48)$$

### Appendix C. Rotational averaging

In this appendix, we consider that the translationally averaged response tensor is expanded over the basis of spherical GTO. We also further assume that the response tensor has been expanded into its trace, antisymmetric and symmetric traceless parts. The irreducible components are noted using the letters  $S\sigma$  ( $S = 0, 1, 2$ ) to make a clear distinction with the total angular momentum  $JM$  that is obtained by coupling the spin and the orbital part of the tensor. The components of the translationally average response tensor are expanded over spherical GTO:

$$\langle \zeta^{S\sigma} \rangle_T(\mathbf{R}) = \sum_i c_{iS\sigma} g_s(l_{iS\sigma}, m_{iS\sigma}, n_{iS\sigma}, \mathbf{r}_{iS\sigma}, \alpha_{iS\sigma}). \quad (49)$$

The components of the translationally and rotationally average tensor are calculated in the following way:

$$\zeta_{SS}^{00}(R) = \int_{\Omega} \langle \zeta \rangle_T(\mathbf{R}) \cdot \mathbf{Y}_{SS}^{00}(\theta, \varphi) d\Omega \\ = \int_{\Omega} \langle \zeta^S \rangle_T(\mathbf{R}) \cdot \mathbf{Y}_{SS}^{00}(\theta, \varphi) d\Omega \\ = \sum_{\sigma} (-1)^{\sigma} \int_{\Omega} \langle \zeta^{S\sigma} \rangle_T(\mathbf{R}) [\mathbf{Y}_{SS}^{00}(\theta, \varphi)]^{-\sigma} d\Omega \\ = \sum_{i\sigma} c_{iS\sigma} (-1)^{\sigma} \int_{\Omega} g_s(l_{iS\sigma}, m_{iS\sigma}, n_{iS\sigma}, \mathbf{r}_{iS\sigma}, \alpha_{iS\sigma}) \\ \times C_{S\sigma, S-\sigma}^{00} Y_{S\sigma}(\theta, \varphi) d\Omega \\ = \sum_{i\sigma} c_{iS\sigma} (-1)^{\sigma} C_{S\sigma, S-\sigma}^{00} (r - r_{iS\sigma})^{n_{iS\sigma}} e^{-\alpha_{iS\sigma}(r - r_{iS\sigma})^2} \\ \times \delta_{S, l_{iS\sigma}}. \quad (50)$$

This last expression is our final result for the radial part of the averaged response tensor.

### Appendix D. Irreducible tensors and tensor spherical harmonics

In this appendix, we provide basic definition of the irreducible formalism and tensor spherical harmonics [13]. Tensor spherical harmonics [28] are obtained through an irreducible tensor product of spherical harmonics  $Y_{lm}$  and the tensorial irreducible basis  $\mathbf{e}_{s\sigma}$  formed by taking irreducible products of the Cartesian vectors

$$\mathbf{Y}_{ls}^{JM} = \{Y^l \otimes \mathbf{e}^s\}^{JM} = \sum_{m\sigma} C_{lm1\sigma}^{JM} Y_{lm} \mathbf{e}_{s\sigma}. \quad (51)$$

Tensor spherical harmonics for  $s = 1$  (vector spherical harmonics) and  $s = 2$  (rank 2 spherical harmonics) are routinely

used in electromagnetism [29] and gravitation theory [30], respectively. The three irreducible basis vectors are given by

$$\mathbf{e}_{1\pm 1} = \mp \frac{1}{\sqrt{2}} (\mathbf{e}_x \pm i\mathbf{e}_y), \\ \mathbf{e}_{10} = \mathbf{e}_z. \quad (52)$$

The five irreducible basis second rank tensors are given by

$$\mathbf{e}_{2\pm 2} = \sqrt{\frac{1}{6}} (\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y \pm 2i\mathbf{e}_x \otimes \mathbf{e}_y), \\ \mathbf{e}_{2\pm 1} = \mp \sqrt{\frac{2}{3}} (\mathbf{e}_z \otimes \mathbf{e}_x \pm i\mathbf{e}_z \otimes \mathbf{e}_y), \\ \mathbf{e}_{20} = \mathbf{e}_z \otimes \mathbf{e}_z. \quad (53)$$

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