



**HAL**  
open science

## From anisotropy of dielectric tensors to birefringence: a quantum mechanics approach

Michel Rérat, Philippe D'arco, Valentina Lacivita, Fabien Pascale, Roberto Dovesi

### ► To cite this version:

Michel Rérat, Philippe D'arco, Valentina Lacivita, Fabien Pascale, Roberto Dovesi. From anisotropy of dielectric tensors to birefringence: a quantum mechanics approach. *Rendiconti Lincei. Scienze Fisiche e Naturali*, 2020, 31 (3), pp.835-851. 10.1007/s12210-020-00931-9 . hal-02907958

**HAL Id: hal-02907958**

**<https://hal.science/hal-02907958>**

Submitted on 2 Oct 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/343238063>

# From anisotropy of dielectric tensors to birefringence: a quantum mechanics approach

Article in *Rendiconti Lincei. Scienze Fisiche e Naturali* · July 2020

DOI: 10.1007/s12210-020-00931-9

CITATIONS

0

READS

74

5 authors, including:



**Michel Rérat**

Université de Pau et des Pays de l'Adour

161 PUBLICATIONS 4,654 CITATIONS

SEE PROFILE



**Philippe d'arco**

Sorbonne Université

71 PUBLICATIONS 2,501 CITATIONS

SEE PROFILE



**Valentina Lacivita**

Università degli Studi di Torino

20 PUBLICATIONS 265 CITATIONS

SEE PROFILE



**Fabien Pascale**

University of Lorraine

41 PUBLICATIONS 2,224 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Ab initio calculation of response properties of periodic systems and implementation of the frequency-dependent CPHF(KS) methods in the Crystal code ([www.crystal.unito.it](http://www.crystal.unito.it)). [View project](#)



Statistics and benchmarking [View project](#)



# From anisotropy of dielectric tensors to birefringence: a quantum mechanics approach

Michel Rérat<sup>1</sup> · Philippe D'Arco<sup>2</sup> · Valentina Lacivita<sup>3,4</sup> · Fabien Pascale<sup>5</sup> · Roberto Dovesi<sup>6</sup>

Received: 11 February 2020 / Accepted: 3 July 2020  
© Accademia Nazionale dei Lincei 2020

## Abstract

The way quantum mechanical ab initio computer codes allow to compute, through perturbation theory (the so-called SC-CP, self-consistent coupled-perturbed scheme), many properties resulting from the interaction of the electric field with a crystalline system is illustrated. The polarizability, which leads to the dielectric tensors as well as to the refractive indices and to the birefringence of materials, is the simplest on this list. Higher order tensors, like the first and second hyperpolarizabilities, can be obtained as well with the CRYSTAL code here used. These properties, resulting from the Taylor expansion of the total energy of the solid as a function of the electric field, belong to a large family of phenomena generated by combining in different ways the frequencies of the fields. Second-harmonic generation (SHG), Pockels effect, intensity-dependent refractive index (IDRI), and other quantities now accessible to experiment can be computed at a relatively low cost and with high accuracy.

**Keywords** Refractive index · Birefringence · (Non)linear electric susceptibility tensor · Anisotropy · Quantum mechanical simulation · CRYSTAL code · Gaussian-type basis set

## 1 Introduction

In this contribution, we illustrate the way modern quantum mechanical methods allow to compute the (hyper)polarizability tensors and, consequently, optical properties such as the refractive index and birefringence, through which the anisotropy of the physical properties of crystalline compounds manifests itself.

The properties mentioned above can be obtained by investigating the interaction of the electromagnetic field with a periodic infinite system (the model implies, without serious consequences, that the crystalline compound is infinite).

The equations describing this interaction can be formulated at various levels (for example: relativistic or non-relativistic quantum mechanics). As none of these equations can be solved exactly, many approximations must be introduced, whose importance should be discussed carefully, and one should possibly verify numerically how severe these approximations are.

In a very broad sense, all these equations are solved by performing at various steps series expansions, so that the differential equations transform in matrix equations.

This essentially requires: (a) to compute matrix elements (these, in turn, are the sum of integrals, many of which are

This paper is the peer-reviewed version of a contribution presented at the Conference on Anisotropic Properties of Matter, organized by Giovanni Ferraris and held at Accademia Nazionale dei Lincei in Rome, October 16–17, 2019.

✉ Michel Rérat  
michel.rerat@univ-pau.fr

<sup>1</sup> Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, 2 av. président P. Angot, 64053 Pau, France

<sup>2</sup> Sorbonne Université, CNRS-INSU, IStEP UMR 7193, 75005 Paris, France

<sup>3</sup> Advanced Materials Lab, Samsung Research America, 10 Wilson Rd., Cambridges, MA 02138, USA

<sup>4</sup> Sorbonne Université, CNRS, IMJ UMR 7586, 75005 Paris, France

<sup>5</sup> Université de Lorraine-Nancy, CNRS, Laboratoire de Physique et Chimie Théoriques, UMR 7019, Vandoeuvre-les-Nancy, France

<sup>6</sup> Dipartimento di Chimica, Nanostructured Interfaces and Surfaces (NIS) Centre of Excellence, Università di Torino, Via P. Giuria 7, 10125 Turin, Italy

42 bielectronic four center six dimensional integrals); (b) sum,  
43 multiply, and diagonalize matrices that can easily reach very  
44 large dimensions ( $10^3$ – $10^6$ , as typical cases).

45 The larger the matrices, the more accurate the calculation.

46 Obviously, this kind of linear algebra requires the use of  
47 computers (clusters of PC) or supercomputers containing  
48  $10^2$ – $10^4$  processors.

49 The starting point for describing the crystalline system is  
50 the (stationary, or time-independent) Schrödinger's equation:

$$51 \hat{H}\Psi = \mathcal{E}\Psi, \quad (1)$$

52 where  $\hat{H}$  is an operator, called Hamiltonian in memory of  
53 classical mechanics developed by Lagrange (1736–1813)  
54 and then Hamilton (1805–1865), and  $\mathcal{E}$  the energy associ-  
55 ated to the wavefunction  $\Psi$ .

56 The real limit of this equation is that  $\hat{H}$  and  $\Psi$   
57 depend on many variables as atomic positions, that is  
58  $\Psi \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$ . In the case of an infinite crystalline  
59 system,  $N$  goes to infinity. But also for a molecule like, say,  
60 benzene, containing 12 atoms and 42 electrons, for a total  
61 of 162 Cartesian coordinates (plus the spin), the Schrödinger's  
62 equation cannot be solved exactly, and its approximate  
63 solution requires a huge amount of skills and computational  
64 effort. We will not dwell on the techniques, hypotheses, and  
65 approximations that bring this intractable problem to some-  
66 thing that can be tackled. The interested reader can refer to  
67 several excellent textbooks covering quantum mechanics and  
68 computational chemistry methods. We simply mention that  
69 these approximations bring to the so-called Hartree–Fock or  
70 Kohn–Sham methods, in which a single particle (say elec-  
71 tron) is moving in the field created by all the other electrons  
72 (whose wavefunction is unknown; mean field theory). This  
73 implies, in turn, that these equations must be solved through  
74 a self-consistent field (SCF) scheme.

75 We can now suppose that we are able to describe with  
76 reasonable accuracy the ground state of a crystalline system.

77 We are then faced with the problem of the description  
78 of the electromagnetic field, and of its interaction with the  
79 solid. This interaction is described through a well-known  
80 tool of quantum mechanics, namely the perturbation theory,  
81 that takes the form of a Taylor expansion of the system's  
82 energy in powers of the electric field. As usual, the series is  
83 truncated after a few terms due to (a) computational costs  
84 and (b) hopefully, the rapid convergence. Also in this case,  
85 the solution of the resulting equations requires an iterative  
86 scheme. At the very end, the crucial points (crucial due to  
87 numerical accuracy and computational cost) are: evaluation  
88 of multicenter integrals and multiplication of very large  
89 matrices.

90 We are then considering a crystalline solid, and an elec-  
91 tric field operating on it. What is the information that can be  
92 obtained as a response of the system to this perturbation? Let  
93

us consider the Taylor expansion of the total bulk energy of  
the system with respect to the field amplitude  $\mathbf{E}_0$ , truncated  
to the fourth order:

$$94 \mathcal{E} = \mathcal{E}_0 - \boldsymbol{\mu}_0 \cdot \mathbf{E}_0 - \frac{1}{2!} \boldsymbol{\alpha}_0 \mathbf{E}_0 \otimes \mathbf{E}_0 - \frac{1}{3!} \boldsymbol{\beta}_0 \mathbf{E}_0 \otimes \mathbf{E}_0 \otimes \mathbf{E}_0 \quad 97$$

$$98 - \frac{1}{4!} \boldsymbol{\gamma}_0 \mathbf{E}_0 \otimes \mathbf{E}_0 \otimes \mathbf{E}_0 \otimes \mathbf{E}_0, \quad (2)$$

99 where  $\boldsymbol{\mu}_0$ ,  $\boldsymbol{\alpha}_0$ ,  $\boldsymbol{\beta}_0$ , and  $\boldsymbol{\gamma}_0$  are the permanent dipole moment,  
100 polarizability, and first and second hyperpolarizabilities  
101 of the free system, respectively (the conventional nega-  
102 tive sign is such that the dipole moment is defined as the  
103 sum over the charges multiplied by their position, and such  
104 that the polarizability of the ground state is positive). The  
105 symbol  $\otimes$  indicates the outer product of vectors. Given  
106 the electric field conversion coefficient from the atomic  
107 units (a.u.) system to the international system of units  
108 (SI): 1 a.u. =  $5.14 \times 10^{11}$  Vm $^{-1}$ , a large static field of say  
109 50 kVcm $^{-1}$  (maximum field amplitude that can be applied  
110 with electrodes at the surface of a slab before electric break-  
111 down), is smaller than  $10^{-5}$  a.u.. If we apply a field of this  
112 amplitude to a molecule, say water, with a polarizability  
113 equal to  $\sim 10$  bohr $^3$  (the polarizability unit is equivalent to  
114 a volume in a.u.), the energy variation due to the polariza-  
115 tion would be equal to  $10^{-9} E_h$ . As the ratio between the  
116 terms appearing in Eq. 2 ( $\boldsymbol{\beta}_0/\boldsymbol{\alpha}_0$ ,  $\boldsymbol{\gamma}_0/\boldsymbol{\beta}_0$ ) is generally smaller  
117 than  $10^3$  a.u., to be multiplied by an additional field intensity  
118 of  $10^{-5}$ , it is clear that contributions approach rapidly the  
119 numerical accuracy limit of quantum mechanical calcula-  
120 tions. This is why,  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  coefficients have been con-  
121 sidered in the past of low interest, and terms as  $\boldsymbol{\delta}_0$ , corre-  
122 sponding to power five of  $\mathbf{E}_0$ , have been neglected in Eq. 2.  
123 However, if the expanded quantity is not the total energy,  
124 but some higher term evaluated analytically, then the power  
125 of  $\mathbf{E}_0$  for obtaining  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  is lower. This is the case, for  
126 example, when the polarizability  $\boldsymbol{\alpha}_0$  is computed analytically,  
127 with a reduction by 2 of the power of  $\mathbf{E}_0$ . Moreover,  
128 lasers with much higher intensity than static electric fields  
129 are now available, which can allow to access experimen-  
130 tally many non-negligible second- and third-order non-linear  
131 optical (NLO) effects.

132 It should be stressed that Eq. 2 can provide a lot of  
133 information:

- 134 (a) as  $\mathbf{E}_0$  is a vector with three components,  $E_x$ ,  $E_y$ , and  $E_z$ ,  
135 it turns out that  $\boldsymbol{\mu}_0$ ,  $\boldsymbol{\alpha}_0$ ,  $\boldsymbol{\beta}_0$ , and  $\boldsymbol{\gamma}_0$  are tensors of rank 1,  
136 2, 3, and 4, respectively, whose components can vary  
137 from case to case, allowing access to important specific  
138 features.
- 139 (b) The electric fields appearing in Eq. 2 can be different  
140 from each other (say  $\mathbf{E}_1$ ,  $\mathbf{E}_2$  ...), and combined in dif-  
141 ferent ways.

- (c) Obviously, the various electric fields can depend on frequency as in light radiation,  $\mathbf{E} \equiv \mathbf{E}(\omega) = \mathbf{E}_0 \cos(\omega t)$  with the angular  $\omega$ -frequency of the corresponding photon ( $\hbar\omega$  with  $\hbar = h/2\pi$ ,  $h$  being the Planck constant equal to  $6.63 \times 10^{-34}$  Js), further increasing the number of possible ways of perturbing the system. For example, in the second-harmonic generation (SHG) experiments, interaction of light with matter can provide one scattered photon of energy  $\hbar 2\omega$  from two photons of energy  $\hbar\omega$ , the intensity of the scattering light depending on the frequency-dependent first hyperpolarizability,  $\beta(-2\omega; \omega, \omega)$ , of the material, as we will see later on.
- (d) As a corollary to point (c), the frequency can be used for perturbing both nuclei and electrons, or just the latter.

The following section will deepen some of the main topics introduced here.

## 2 Methods

### 2.1 Dipole moment and (hyper)polarizability

#### 2.1.1 Definitions

The dipole moment  $\boldsymbol{\mu}$  of a finite system is a vector defined, in the atomic unit system, as:

$$\boldsymbol{\mu} = \sum_N Z_N \mathbf{r}_N - \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where the absolute value of the electron charge is equal to 1 ( $e = -1$  a.u.).  $Z_N$  and  $\mathbf{r}_N$  are the nuclear charge and position of the  $N$ th atom, and  $\rho(\mathbf{r})$  is the electron charge density in  $\mathbf{r}$ . For a given geometry,  $Z_N$  and  $\mathbf{r}_N$  are fixed, and the value of the dipole moment can be obtained if the electron density is known in the whole space. In quantum chemistry, this latter, which is the square of a wave function,  $\Psi$ , describing the electronic state of the system (generally its ground state) can be obtained by solving the time-independent Schrödinger's equation (see Eq. 1). Using Dirac's notation,  $\int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}$  in Eq. 3 can now be replaced by  $\langle 0 | \mathbf{r} | 0 \rangle$  where  $\langle 0 |$  and  $| 0 \rangle$  represent the bra and ket of the ground state.

In the presence of a time-dependent electromagnetic ( $\mathbf{E}(\mathbf{r}, t)$ ,  $\mathbf{B}(\mathbf{r}, t)$ ) field, the expression of  $\hat{H}$  becomes:

$$\hat{H} = \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t) \right)^2 + eU(\mathbf{r}, t) + V_C(\mathbf{r}), \quad (4)$$

where  $\mathbf{p}$  and  $\mathbf{r}$  are the momentum and position of the electron,  $m$  its mass ( $m = 1$  a.u.),  $c$  the speed of light ( $c = 137$  a.u.), and  $V_C$  the Coulomb potential. The electromagnetic field is

defined from the vector  $\mathbf{A}(\mathbf{r}, t)$  and scalar  $U(\mathbf{r}, t)$  potentials via Maxwell's equations:

$$\mathbf{E}(\mathbf{r}, t) = - \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} - \nabla U(\mathbf{r}, t) \quad (5)$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (6)$$

and there is an infinite number of ( $\mathbf{A}(\mathbf{r}, t), U(\mathbf{r}, t)$ ) couples describing one electromagnetic field. Obviously, the solutions of the time-dependent Schrödinger's equation must be independent from the choice of the so-called gauge. This is indeed the case of the energy  $E$ -eigenvalue as well as of  $|\Psi(\mathbf{r}, t)|^2$ . Only the phase of the wave function depends on the choice of the gauge.

For a static electric field:  $\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 e^{i\mathbf{q} \cdot \mathbf{r}}$  with a small wave number:  $q = 2\pi/\lambda$  compared to  $\mathbf{r}$  (i.e., for  $\lambda$ -wavelength much larger than the size of the studied system:  $\lambda \gg 1 \text{ \AA}$ ),  $\mathbf{E}(\mathbf{r})$  is generally defined from the scalar potential only as follows:

$$\mathbf{E}(\mathbf{r}) = -\nabla U(\mathbf{r}), \quad (7)$$

which leads for a constant field  $\mathbf{E}_0$  to:

$$\hat{H} = \frac{\mathbf{p}^2}{2m} + V_C(\mathbf{r}) - e\mathbf{r} \cdot \mathbf{E}_0 = \hat{H}_0 - e\mathbf{r} \cdot \mathbf{E}_0 \quad (8)$$

in the electric dipole moment approximation for finite systems (OD or molecules),  $\hat{H}_0$  being the Hamiltonian operator of the unperturbed system.

The energy  $\mathcal{E}$  of the molecule in presence of the  $\mathbf{E}_0$ -field can be developed as a Taylor series as shown in Eq. 2; similarly, for the dipole moment, we have:

$$\boldsymbol{\mu} = - \frac{d\mathcal{E}}{d\mathbf{E}_0} = \boldsymbol{\mu}_0 + \boldsymbol{\alpha}_0 \mathbf{E}_0 + \frac{1}{2!} \boldsymbol{\beta}_0 \mathbf{E}_0 \otimes \mathbf{E}_0 + \frac{1}{3!} \boldsymbol{\gamma}_0 \mathbf{E}_0 \otimes \mathbf{E}_0 \otimes \mathbf{E}_0 + \dots, \quad (9)$$

where  $\boldsymbol{\mu}_0$  is the permanent dipole moment of the molecule, the linear response  $\boldsymbol{\alpha}_0$  is called the polarizability, and  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  are the first and second hyperpolarizabilities. The previous electric responses to the electric field are intrinsic properties of the molecule: they are equal to the first, second, and third derivatives of the induced dipole moment ( $\boldsymbol{\mu} - \boldsymbol{\mu}_0$ ) with respect to the field  $\mathbf{E}_0$ , at zero field ( $\mathbf{E}_0 \rightarrow \mathbf{0}$ ). Moreover, being  $\boldsymbol{\mu}_0$  and  $\mathbf{E}_0$  vectors,  $\boldsymbol{\alpha}_0$ ,  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  are tensors of rank 2, 3, and 4, respectively.

In the case of a frequency-dependent electric field ( $\mathbf{E}(\omega) = \mathbf{E}_0 \cos \omega t$ ), the linear term of the dipole moment induced by the oscillating field is oscillating at the same frequency of the field (forced oscillation if the field frequency is small compared to proper resonance frequencies of the system) leading to a frequency-dependent polarizability,  $\boldsymbol{\alpha}(\omega)$ . For a molecule in its electronic ground state ( $|0\rangle$ ),



232 the "dynamic" polarizability is a sum of two contributions  
233 that can be separately calculated in the Born–Oppenheimer  
234 approximation:

235 1. The electronic ( $\alpha^e$ ) contribution, for a fixed ( $\mathbf{r}_N$ ) geom-  
236 etry:

$$237 \alpha^e(\omega) = \sum_{n \neq 0}^{\infty} 2\omega_n \frac{\boldsymbol{\mu}_n \otimes \boldsymbol{\mu}_n}{\omega_n^2 - \omega^2}, \quad (10)$$

238 where  $\omega_n = \mathcal{E}_n - \mathcal{E}_0$  are the allowed transition energies  
239 from the  $|0\rangle$ -ground to  $|n\rangle$ -excited electronic states with  
240  $\mathcal{E}_0$  and  $\mathcal{E}_n$  as corresponding eigenvalues of the unperturbed  
241 Hamiltonian operator  $\hat{H}_0$  (if we are interested in the polarizability  
242 of the ground state) and  $\boldsymbol{\mu}_n = \langle 0|\mathbf{r}|n\rangle$   
243 is the corresponding transition dipole moment.

244 The associated mean value oscillator strengths:

$$245 f_n = \frac{2}{3}\omega_n \langle 0|\mathbf{r}|n\rangle^2 \quad (11)$$

246 are such that  $\sum_n f_n$  is equal to the number of electrons  
247 involved in these transitions, and the  $(\omega_n, f_n)$  couples  
248 reproduce the UV–visible spectrum.

249 See the work of Orr and Ward (1971) for the expres-  
250 sion of hyperpolarizabilities.

251 2. The ionic or nuclear relaxation ( $\alpha^{nr}$ ) contribution:

$$252 \alpha^{nr}(\omega) = \sum_{i=1}^{3N-6} \frac{\boldsymbol{\sigma}_i \otimes \boldsymbol{\sigma}_i}{\omega_i^2 - \omega^2}, \quad (12)$$

253 where  $\omega_i$  is the frequency of the normal mode ( $Q_i$ ) and  
254  $\boldsymbol{\sigma}_i$  the Born charge ( $d\boldsymbol{\mu}_0/dQ_i$  with  $\boldsymbol{\mu}_0$  as defined in Eq. 3  
255 at zero field) obtained at the equilibrium geometry. The  
256  $(\omega_i, \boldsymbol{\sigma}_i)$  couples reproduce the infrared (IR) spectrum.

257 We refer to the work of Kirtman and Luis (2010) for  
258 the treatment of the vibrational hyperpolarizabilities that  
259 can be evaluated from the IR and (hyper) Raman spectra.

260  $\alpha^{nr}$  is zero in purely covalent materials as diamond or sili-  
261 con, and also negligible for other ionic materials if the field  
262 frequency ( $\omega$ ) corresponds to the UV–visible range of  
263 energy  $\omega \gg \omega_i$ . Indeed, the Born charge  $d\boldsymbol{\mu}_0/dQ_i$ , which is  
264 actually a charge divided by the square root of ion mass, is  
265 small with respect to 1 a.u., and  $\boldsymbol{\sigma}_i^2/(\omega_i^2 - \omega^2) \simeq -\boldsymbol{\sigma}_i^2/\omega^2$ ,  
266 which is then negative, becomes very small in absolute val-  
267 ues compared to the static vibrational polarizability contri-  
268 bution:  $\boldsymbol{\sigma}_i^2/\omega_i^2$ .

269 Also the vibrational contribution to  $\beta$  and  $\gamma$  can be  
270 neglected in the UV–visible frequency range for the same  
271 reason as for  $\alpha$ , if all the external fields are frequency-  
272 dependent. The exception is the particular case of the inten-  
273 sity-dependent refractive index, IDRI, a process depending  
274 on  $\boldsymbol{\gamma}(-\omega; \omega, -\omega, \omega)$ , that includes terms with opposite sign

275 phases,  $\pm\omega$ , generating then a static field and a vibrational  
276 contribution.

## 2.1.2 Calculation of the microscopic response properties

277 The electronic contribution to the polarizability (Eq. 10) is a  
278 second-order perturbation energy, the expression of which is  
279 a sum extended to an infinite number of excited state terms,  
280 a series which generally converges very slowly. Moreover,  
281 it also depends on the continuum. For example, if we use  
282 all the true (and well known) discrete spectral states of the  
283 H atom, its polarizability value is less than  $4 \text{ bohr}^3$ , while  
284 its exact value is  $9/2 \text{ bohr}^3$  (without taking into account the  
285 relativistic effect) (Coulson 1941; McDowell 1976; Traini  
286 1996; Bishop 1999).

287 Fortunately, it is not necessary to know all the excited  
288 discrete and continuum states of the electronic system to  
289 obtain a "good" static polarizability value, or dynamic polar-  
290 izabilities for a field frequency smaller than the first reso-  
291 nance one. The coupled-perturbed Hartree–Fock (CPHF)  
292 method proposed by Hurst et al. (1988), consisting in the  
293 independent-particle model using relaxed occupied and vir-  
294 tual orbitals via a self-consistent process in the presence of  
295 the external field, generally leads to results in good agree-  
296 ment with the experiments, in particular when a density  
297 functional theory (DFT) Hamiltonian with a percentage of  
298 the exact or Hartree–Fock (HF) non-local exchange potential  
299 is used, as is the case of the hybrid B3LYP (Becke 1993;  
300 Lee et al. 1988) functional (20% of HF exchange). Indeed,  
301 response properties which are n-order perturbation energies  
302 depend strongly on the band gap (which determines the low-  
303 est transition energy values,  $\omega_n \geq \text{gap}$ , on the denominator  
304 of Eq. 10 for electronic polarizability, and of hyperpolariz-  
305 abilities), generally too large with HF (Evarestov 2007) and  
306 too small with pure DFT (Yakovkin and Dowben 2007), but  
307 reasonably described by hybrids (Garza and Scuseria 2016).

## 2.1.3 Infinite periodic systems

312 Expression 8 of the Hamiltonian, that includes the position  
313 operator,  $\mathbf{r}$ , as the perturbation operator associated to the  
314 external field, comes from the dipole moment approximation  
315 that can be used for finite systems (molecules) in the pres-  
316 ence of a constant field, or a field with a large  $\lambda$  wavelength  
317 with respect to the size of the electronic system ( $\lambda \gg 1 \text{ \AA}$ ).

318 For infinite periodic systems, the electric potential  $\mathbf{r} \cdot \mathbf{E}_0$   
319 becomes infinite at  $(\pm\infty)$ , where the electronic density  $\rho$  is  
320 finite, so that the wavefunction is not square summable in  
321 Eq. 3. Moreover, infinite periodic systems described by sym-  
322 metry translated cells and for which the crystalline orbitals  
323 (CO) are combinations of Bloch functions following Born  
324 von Karman (BVK) conditions (last cell in each direction is  
325 bound with the first one) have an ill-defined dipole moment.

327 Indeed, what is the dipole moment of a polymer  $(AB)_{n \rightarrow \infty}$ ,  
 328 that of AB:  $-(A-B)-(A-B)-(A-B)-$  or the one of BA:  
 329  $-(A)-(B-A)-(B-A)-(B)-$  ?

330 Actually  $\mathbf{r}$ , which is a non-periodic potential, is not Her-  
 331 mitian in the BVK CO basis set depending of the  $\mathbf{k}$  points of  
 332 the reciprocal space. Then, we must restart from the expres-  
 333 sion of an external electric field described by a scalar potential  
 334 gauge:  $\mathbf{E} = \mathbf{E}_0 e^{i\mathbf{q}\cdot\mathbf{r}}$ , where  $\mathbf{E}_0$  is the field amplitude and  $q$  its  
 335 wave number  $2\pi/\lambda$ , and determine dipole moment transitions  
 336 between  $i(\mathbf{k})$  and  $j(\mathbf{k}')$  COs involved in the field perturbation  
 337 at the  $\mathbf{q} \rightarrow \mathbf{0}$  limit for a constant field. Using the momentum  
 338 conservation:  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ , it follows that the dipole moment  
 339 operator becomes (Blount et al. 1962; Otto 1992; Rérat et al.  
 340 2008):

$$341 \hat{Q}_k = \mathbf{r} + i\nabla_k = -ie^{-i\mathbf{k}\cdot\mathbf{r}}\nabla_k e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (13)$$

343 and the perturbative Hamiltonian (multiplied by the constant  
 344  $\mathbf{E}_0$  field) is Hermitian and remains block diagonal in the  
 345 reciprocal space for  $\lambda \gg 1 \text{ \AA}$ .

346 The basic equations of the self-consistent coupled-per-  
 347 turbed (SC-CP) computational scheme for periodic systems  
 348 can be found in Ferrero et al. (2008a, b) for the CPHF calcula-  
 349 tion of (hyper)polarizabilities, adapted to Kohn–Sham Hamil-  
 350 tonian (CPKS) in Orlando et al. (2010) and to frequency-  
 351 dependent electric fields in Ferrari et al. (2015), Rérat et al.  
 352 (2015), Maschio et al. (2015), whereas many numerical exam-  
 353 ples are reported in Sect. 3.

## 354 2.2 Refractive index

355 In this section, we are going to look at the refractive index of  
 356 materials, which is a macroscopic property depending on the  
 357 (hyper)polarizability described in the previous section, as we  
 358 will see further. Let us look first at the definition of this optical  
 359 property and then at the resulting birefringence of materials.

### 360 2.2.1 Definition

361 Electric induction ( $\mathbf{D}$ ) and magnetic excitation ( $\mathbf{H}$ ) fields are  
 362 related to the frequency( $\omega$ )-dependent electromagnetic ( $\mathbf{E}, \mathbf{B}$ )  
 363 field as follows (Condon 1937):

$$364 \mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E} - \frac{\boldsymbol{\xi}}{c} \frac{\partial \mathbf{H}}{\partial t} \quad (14)$$

$$366 \mathbf{B} = \mu_r \mu_0 \mathbf{H} + \frac{\boldsymbol{\xi}}{c} \frac{\partial \mathbf{E}}{\partial t}, \quad (15)$$

368 where  $\epsilon_r$  and  $\mu_r$  are the relative electric permittivity and  
 369 magnetic permeability (matrices) of the medium, respec-  
 370 tively;  $\epsilon_0$  and  $\mu_0$  are the permittivity and permeability (con-  
 371 stants) of the vacuum, such that  $\mu_0 \epsilon_0 c^2 = 1$ ; and  $\boldsymbol{\xi}$  is the

372 chirality (matrix) responsible of the rotation angle of a polar-  
 373 ized electromagnetic field.

374 Then, for materials with  $\mu_r \simeq \mathbf{1}$  (low magnetic perme-  
 375 ability) and  $\boldsymbol{\xi} = \mathbf{0}$  (no chirality), the refractive index is  
 376 (Condon 1937):

$$377 \mathbf{n} = \left( (\mu_r \epsilon_r)^{-\frac{1}{2}} \pm \omega \boldsymbol{\xi} \right)^{-1} \simeq \sqrt{\epsilon_r}. \quad (16)$$

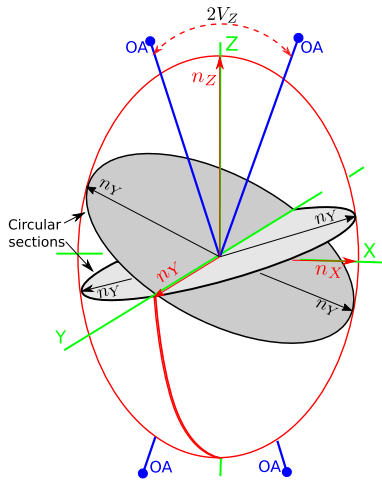
### 379 2.2.2 Optical indicatrix and birefringence

380 As seen above, the relative dielectric tensor  $\epsilon_r$  is a second-  
 381 rank symmetric tensor usually represented by a Hermitian  
 382 matrix. This matches an ellipsoid (Nye 1985), the *optical*  
 383 *indicatrix*, whose equation is:

$$384 \frac{X^2}{n_X^2} + \frac{Y^2}{n_Y^2} + \frac{Z^2}{n_Z^2} = 1$$

385 and with semi-axis lengths given by the square roots of the  
 386 dielectric tensor eigenvalues,  $n_i = \sqrt{\epsilon_i}$  ( $i = X, Y, Z$ ), corre-  
 387 sponding to the *principal refractive indices* of the medium.  
 388 We will assume that the indices along the semi-axis  $X, Y, Z$ ,  
 389 are ordered by increasing value.

390 Hence, the phenomenon of *birefringence* is estimated  
 391 as the difference  $\delta = n_Z - n_X$ . In principle, all crystals are  
 392 birefringent and the specific indicatrix properties depend  
 393 on the crystal symmetry. However, some special direc-  
 394 tions—the *optical axes*—exist which select as many  
 395 circular sections within the indicatrix. For cubic miner-  
 396 als, which are optically isotropic, the optical indicatrix  
 397 (see Fig. 1) is a sphere (null birefringence) defined by  
 398 a unique refractive index  $n$ . The uniaxial optical indica-  
 399 trix of tetragonal, hexagonal, or trigonal minerals is an  
 400 ellipsoid of revolution characterized by two independent  
 401 semi-axis of length  $n_\omega$  and  $n_\epsilon$ . The axis of revolution of the  
 402 indicatrix parallels the  $c$ -direction of the mineral and cor-  
 403 responds to  $n_\epsilon$ . Such ellipsoid possesses a single circular  
 404 section perpendicular to the  $c$ -direction which corresponds  
 405 to the optical axis. The birefringence is  $\delta = |n_\epsilon - n_\omega|$ . If  
 406  $n_\epsilon > n_\omega$  ( $n_\epsilon = n_Z, n_\omega = n_X = n_Y$ ) the indicatrix and the cor-  
 407 responding mineral are said uniaxial positive. If  $n_\epsilon < n_\omega$   
 408 ( $n_\epsilon = n_X, n_\omega = n_Y = n_Z$ ), the indicatrix and the corre-  
 409 sponding mineral are said uniaxial negative. Any other  
 410 mineral is *biaxial*, having an optical ellipsoid with two cir-  
 411 cular sections (and as many optical axes) of indices  $n_Y$  (see  
 412 Fig. 1).  $n_X$  and  $n_Z$  lie on the plane of the optical axes and  
 413 bisect the angles between them. Depending on whether the  
 414 acute angle between the optical axes ( $2V$ ) is bisected by  $n_Z$   
 415 ( $2V = 2V_Z$ ) or by  $n_X$  ( $2V = 2V_X$ ), the crystal is said to be  
 416 *positive* or *negative*.  $2V_Z + 2V_X = \pi$ . The following equa-  
 417 tion defines the relationship between  $V$  and  $n_X, n_Y$  and  $n_Z$ :  
 418



**Fig. 1** Representation of the indicatrix of a positive biaxial crystals. The directions of the principal axes of the ellipsoid X, Y, and Z are represented by a thick green line, and the associated red thin arrows indicate the corresponding refractive indices  $n_X$ ,  $n_Y$ , and  $n_Z$ . The grey surfaces are the circular sections of the indicatrix, and their radius is constant and equals  $n_Y$ . The normals to the circular sections or optical axis (OA) form the acute  $2V_Z$  angle bisected by the Z semi-axis. For uniaxial crystals  $n_X = n_Y$ , usually indicated as  $n_o$ , and  $n_Z$  is indicated as  $n_e$ ; the two circular sections merge in a single one orthogonal to Z

$$\cos V = \frac{n_X}{n_Y} \sqrt{\frac{n_Z^2 - n_Y^2}{n_Z^2 - n_X^2}}$$

### 2.2.3 Non-linear optics and birefringence

Intense electric fields can also provide birefringence as demonstrated in the following.

Equation 14 for  $\xi = \mathbf{0}$  can also be written as follows:

$$\mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E} = \epsilon_0 \mathbf{E} + \mathbf{P}, \tag{17}$$

where the polarization vector,  $\mathbf{P}$ , is the dipole moment per unit volume induced by the macroscopic field, and can be developed in a Taylor series as follows:

$$\mathbf{P} = \epsilon_0 (\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} \otimes \mathbf{E} + \chi^{(3)} \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} + \dots), \tag{18}$$

where  $\chi^{(n)}$  are the (non)linear electric susceptibility tensors of rank  $(n + 1)$ , the units of which are the inverse of field to the  $(n - 1)$ th power.

Let us consider the field  $\mathbf{E}$  produced by the light wave of frequency  $\omega$  together with an external static electric field  $\mathbf{E}_0$ :

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_\omega \cos \omega t, \tag{19}$$

where  $\mathbf{E}_\omega$  is the vector amplitude of the wave. Then, a non-zero component value of  $\chi^{(2)}$  leads to an additive term proportional to  $E_0$ -modulus in the expression of the polarization

vector which oscillates with the same  $\omega$  frequency as the electromagnetic field:

$$\mathbf{P}(\omega) = \epsilon_0 (\chi_{(-\omega;\omega)}^{(1)} + 2\chi_{(-\omega;\omega,0)}^{(2)} \mathbf{E}_0) \mathbf{E}_\omega \cos \omega t, \tag{20}$$

and induces a linear variation of the refractive index with respect to the modulus of  $\mathbf{E}_0$ :

$$\mathbf{n}(\omega) = \sqrt{\mathbf{1} + \chi_{(-\omega;\omega)}^{(1)} + 2\chi_{(-\omega;\omega,0)}^{(2)} \mathbf{E}_0} \approx \mathbf{n}_0(\omega) + \mathbf{n}_1(\omega) \mathbf{E}_0$$

with

$$\mathbf{n}_0(\omega) = \sqrt{\mathbf{1} + \chi_{(-\omega;\omega)}^{(1)}} \text{ and } \mathbf{n}_1(\omega) = \chi_{(-\omega;\omega,0)}^{(2)} / \mathbf{n}_0(\omega).$$

This Pockels effect responsible of the birefringence:  $\Delta \mathbf{n} = \mathbf{n}_1 \mathbf{E}_0$ , depends on the odd rank tensor,  $\chi^{(2)}$ , which is null for materials with an inversion symmetry. However, the birefringence of centrosymmetric materials can be seen if they own a large third-order non-linear  $\chi^{(3)}$  susceptibility (tensor of rank four) and for intense electric fields. Indeed, it comes from the quadratic term in  $\mathbf{E}$  in the polarization vector expression (Eq. 18). In the intensity-dependent refractive index (IDRI) Kerr effect (see Boyd 2003), an intense beam of light in the crystal can itself provide the modulating electric field:

$$\mathbf{E} = \mathbf{E}_\omega \cos \omega t = \frac{1}{2} \mathbf{E}_\omega (e^{i\omega t} + e^{-i\omega t})$$

without the need for an external field to be applied. The product of frequency-dependent fields leads again to a polarization vector oscillating with the same frequency as the laser field:

$$\mathbf{P}(\omega) = \epsilon_0 \left( \chi_{(-\omega;\omega)}^{(1)} + \frac{3}{4} \chi_{(-\omega;\omega,-\omega,\omega)}^{(3)} \mathbf{E}_\omega^2 \right) \mathbf{E}_\omega \cos \omega t, \tag{23}$$

and then, we have:

$$\mathbf{n}(\omega) \approx \mathbf{n}_0(\omega) + \frac{3}{8n_0(\omega)} \chi_{(-\omega;\omega,-\omega,\omega)}^{(3)} \mathbf{E}_\omega^2 \approx \mathbf{n}_0(\omega) + \mathbf{n}_2(\omega) \mathbf{I}$$

with  $\mathbf{I}$  the light intensity. In that case, the birefringence is given by  $\mathbf{n}_2$ , i.e., by the IDRI-Kerr non-linear electric  $\chi_{(-\omega;\omega,-\omega,\omega)}^{(3)}$  susceptibility.

A recent application referring to yttria-stabilized zirconia can be found in Marcaud et al. (2020). Several other NLO processes also appear when combining the Taylor development of the polarization vector shown in Eq. 18 with the field expression given in Eq. 19 (see Saleh and Teich 1991; Boulon 2001), as SHG linked to  $\chi^{(2)}(-2\omega;\omega, \omega)$  and third harmonic generation (THG) linked to  $\chi^{(3)}(-3\omega;\omega, \omega, \omega)$ , but they do not affect the refractive index at  $\omega$ -frequency.



## 2.2.4 Relation between (non)linear susceptibilities and (hyper)polarizabilities

The macroscopic (non)linear optical properties,  $\chi^{(n)}$ , in the expression (Eq. 18) of the polarization vector are linked to the microscopic  $\alpha$ ,  $\beta$ ,  $\gamma \dots$  (hyper)polarizability properties of a unit cell of the material, recalling that  $\mathbf{P}$  is the dipole moment per unit cell volume  $V$  induced by the mean (macroscopic) field ( $\mathbf{E}$ ) felt by the cell, and that can be also developed as follows:

$$\mathbf{P} = \frac{1}{V} \left( \alpha \mathbf{E} + \frac{1}{2!} \beta \mathbf{E} \otimes \mathbf{E} + \frac{1}{3!} \gamma \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} + \dots \right). \quad (25)$$

The relative electric permittivity (or dielectric matrix)  $\epsilon_r$  at zero field is then linked to the polarizability  $\alpha$  of the unit cell:

$$\epsilon_r = \mathbf{1} + \chi^{(1)} = \mathbf{1} + \frac{1}{\epsilon_0} \alpha / V, \quad (26)$$

where  $V$  is the unit cell volume. Similarly, we have:  $\chi^{(2)} = \frac{1}{2!} \frac{1}{\epsilon_0} \beta / V$  and  $\chi^{(3)} = \frac{1}{3!} \frac{1}{\epsilon_0} \gamma / V$ , with  $1/\epsilon_0 = 4\pi$  in atomic units.

It follows that the  $\alpha$ ,  $\beta$ , and  $\gamma$  tensors obtained from the SC-CP calculation discussed in Sect. 2.1.3 for infinite periodic systems allow to determine the (non)linear susceptibilities,  $\chi^{(n)}$ , and the refractive index and birefringence.

## 3 Applications and comparison with experimental data

The examples should provide an idea of the quality of the results that can be obtained by simulation, and in particular with the CRYSTAL code (Dovesi et al. 2017, 2018, 2020).

Before illustrating these examples, it should be mentioned that (obviously) the results depend deeply on the computational parameters; the most important are listed below:

- The variational basis set: in the following examples, a localized Gaussian basis set in split valence or multiple zeta forms, usually including polarization functions, is used. This is in general sufficient to provide accurate results.
- The level of the theory: all calculations are performed at the DFT level, and the most reliable, in our opinion, are obtained with hybrid functionals, containing a fraction of the exact Hartree–Fock exchange. However, as the superiority of one functional with respect to the others is frequently a matter of discussion, in some cases we will compute the same property with various functionals.

- The intrinsic numerical accuracy of the implemented algorithms, that in the CRYSTAL code is very high, so that its influence on the final results can be considered negligible.

One additional point must be underlined, when comparing simulation and experiments: the experimental determinations to be compared with are, in many cases, scarce, or affected by large uncertainty, so that error bars on the two sides (simulation and experiment) should be considered. Just to mention an example: the complete determination of all components of a tensor (and many of the ones mentioned above are third or fourth-order tensors, with many components) requires that the experiment is repeated with different orientations of the crystal, possibly with various polarization of the light. The obtained results are often not directly the specific constant to be inserted in the tensor table, but a linear combination of them generating a system of (linear) equations, whose solution (in particular when small and large numbers are involved) can produce strongly correlated final values. The uncertainty is increased in some cases by the fact that, intrinsically, the experiment is unable to determine the signs of the constants.

One advantage of simulation is that all components of the tensors are determined in a single shot, so that the accuracy of the various terms is the same.

The drawback of simulation is that quantum mechanical calculations refer to  $T = 0$  K, so that the effect of temperature can just be guessed, or evaluated a posteriori with simple and, in general, not very accurate tools.

A few more words about anisotropy: each one of the properties listed above, when referred to a gas or a liquid, reduces to the trace (for order two tensors) or to a few invariants (for higher order tensors). In the solid state, on the contrary, all specificity related to orientation is *contained* in the tensor. Tensors are defined with reference to a cartesian frame (there are rules for defining the orientation of the lattice vectors with respect to the cartesian frame), so that the *constants* take the following form, for a fourth-order tensor:  $T_{ijkl}$ , where  $i, j, k, l$  can be  $x$ , or  $y$  or  $z$ . The first manifestation of anisotropy is that some of these components are null for symmetry reasons. Or, viceversa, if the components that should be null are not, some sort of deformation of the lattice with respect to the ideal situation must be taken into account.

The examples refer to the (hyper)polarizabilities of polyacetylene (PA) for which both electronic and ionic contributions are important, the NLO properties of benchmarks as urea ( $\text{CH}_4\text{N}_2\text{O}$ ) and potassium di-hydrogen phosphate (KDP,  $\text{KH}_2\text{PO}_4$ ), and the birefringence of a series of uniaxial and biaxial minerals.

### 3.1 The case of polyacetylene: the importance of the ionic contribution

The electronic (hyper)polarizabilities (with zero-point averaging included) which are calculated from the SC-CP method described above do not take into account the so-called *pure* vibrational effects, which can be quite important. In the CRYSTAL code, these ionic effects are taken into account analytically for the polarizability,  $\alpha$  (Eq. 12), and for the first hyperpolarizability,  $\beta$  (Eq. 6 of Rérat et al. 2015), from the IR and Raman spectra, but not for  $\gamma$ , the second hyperpolarizability (hyper-Raman data are also required; see Champagne et al. 1997).

Also the dynamic  $\alpha^e(\omega)$  (or  $\alpha^e(-\omega;\omega)$ ) and  $\beta^e(-\omega_\sigma;\omega_1,\omega_2)$  (but not the corresponding  $\gamma^e$ ) can be obtained from CRYSTAL.

The finite field (FF) scheme was implemented in the CRYSTAL code before SC-CP, to compute numerically the static response properties of molecules and periodic systems (see Darrigan et al. 2003). Using then, the finite field nuclear relaxation (FF-NR) scheme of Bishop et al. (1995) that mixes the FF and SC-CP methods, several NLO processes due to the second hyperpolarizabilities can be studied by fitting the Taylor developments of the dipole moment, polarizability, and first hyperpolarizability with respect to the static finite field  $\mathbf{E}$ , at the equilibrium geometry optimized in the presence of the field or not,  $\mathbf{R}_E$  and  $\mathbf{R}_0$  respectively. For example, the Taylor development of the SC-CP (electronic) polarizability is:

$$\alpha_{tu}^e(\mathbf{R}_0, \mathbf{E}) = \alpha_{tu}^e(\mathbf{R}_0, \mathbf{0}) + \sum_v \beta_{tuv}^e E_v + \frac{1}{2} \sum_{v,w} \gamma_{tuvw}^e E_v E_w + \dots \quad (27)$$

$$\alpha_{tu}^e(\mathbf{R}_E, \mathbf{E}) = \alpha_{tu}^e(\mathbf{R}_0, \mathbf{0}) + \sum_v b_{tuv}^\alpha E_v + \frac{1}{2} \sum_{v,w} g_{tuvw}^\alpha E_v E_w + \dots, \quad (28)$$

where:

$$b_{tuv}^\alpha = \beta_{tuv}^e + \beta_{tuv}^{nr}(-\omega;\omega, 0)|_{\omega \rightarrow \infty} \quad (29)$$

$$g_{tuvw}^\alpha = \gamma_{tuvw}^e + \gamma_{tuvw}^{nr}(-\omega;\omega, 0)|_{\omega \rightarrow \infty}. \quad (30)$$

The superscript *nr* indicates the nuclear relaxation approximation for the (field-free) equilibrium vibrational contribution, and the (circular) frequencies of the applied fields are given (as usual) in parentheses, e.g.:  $\beta(0;0,0) = \beta(-\omega_\sigma;\omega_1,\omega_2)$  with static applied fields  $\omega_i = 0$  and  $\omega_\sigma = \omega_1 + \omega_2$ .

Note that the fits on the dipole moment with respect to the static field should lead, in principle, to linear terms identical to the electronic and total static polarizabilities, the latter being the sum of the electronic (Eq. 10) and nuclear relaxation (Eq. 12) contributions to the polarizability:

$$\alpha^\mu = \alpha^{e+nr} = \alpha^e + \alpha^{nr}, \quad (31)$$

since, in either case, only harmonic vibrational terms are included. However, the static hyperpolarizabilities also contain contributions due to anharmonic force constants and anharmonic electrical property derivatives (see, for example, Torrent-Sucarrat et al. 2004). To isolate the nuclear relaxation term, one can either subtract the analytically determined electronic term or calculate the difference between numerical values from the Taylor developments with and without geometry optimization in the presence of the static field. When the geometry is not specified, it is  $\mathbf{R}_0$ ; the omitted frequencies are zero. The subscript  $\omega \rightarrow \infty$  in Eqs. 29 and 30 refers to the infinite optical frequency (high-frequency or UV-visible frequency) approximation. In addition to harmonic terms, first-order anharmonic contributions are also included for  $\gamma^{nr}(-\omega;\omega, 0, 0)|_{\omega \rightarrow \infty}$  with this FF-NR method (see Bishop et al. 1995); for the other two NLO processes,  $\beta^{nr}(-\omega;\omega, 0)|_{\omega \rightarrow \infty}$  and  $\gamma^{nr}(-2\omega;\omega, \omega, 0)|_{\omega \rightarrow \infty}$  (the latter being obtained from fits of  $\beta^e$ ), the first-order anharmonicity terms vanish.

The measured values of non-linear optical properties ordinarily correspond to the sum of vibrational and electronic contributions. In principle, the two may be separated experimentally as well as computationally. For the former, this requires frequency-dependent measurements, as discussed above for  $\alpha$ , and implied when passing for hyperpolarizabilities as suggested by Shelton (1986).

Let us consider now the case of all-trans polyacetylene (PA) (Lacivita et al. 2012), lying in the *xy* plane, with alternating double and single C–C bonds along the *x* periodic direction (a double C–C bond is included within each unit cell). The center of the unit cell is an inversion point (which annihilates odd order energy perturbation terms, i.e.,  $\mu$  and  $\beta$  in our case) and lies on a  $C_2$ -axis perpendicular to the  $\sigma_h^{xy}$  mirror plane, which relates *z* and  $-z$  directions, so that all the components of the  $\alpha$  and  $\gamma$  tensors containing an odd number of *z* indices vanish.

A finite field is applied along the non-periodic directions (*y*, *z*, and mixed *yz*) to obtain the various non-zero independent tensor components of the vibrational (hyper)polarizabilities.  $\gamma$  is a fourth-order tensor consisting, in principle, of  $3^4 = 81$  components,  $\gamma_{tuvw}$ . Several components are, however, null or equivalent either by point symmetry or permutation of indices, the latter depending on the number of static field indices. For example, in the case of  $\gamma_{tuvw}^{nr}(-\omega;\omega, 0, 0)|_{\omega \rightarrow \infty}$ , only the permutations  $\mathcal{P}_{t,u}$  (associated with the  $\omega \rightarrow \infty$

676 limit) and  $\mathcal{P}_{V,W}$  (between two static fields) leave the prop- 706  
 677 erty invariant. According to the number ( $m = 4, 2$  or  $1$ ) of 707  
 678 static fields, there are three nuclear relaxation contributions 708  
 679 to the second hyperpolarizability: 709

680 (a)  $\gamma_{4,tuvw}^{nr} = \gamma_{TUVW}^{nr}(0;0,0,0)$ , 710  
 681 (b)  $\gamma_{2,tuvw}^{nr} = \gamma_{tuVW}^{nr}(-\omega;\omega,0,0)|_{\omega \rightarrow \infty}$  711  
 682 and 712  
 683 (c)  $\gamma_{1,tuvw}^{nr} = \gamma_{tuVW}^{nr}(-2\omega;\omega,\omega,0)|_{\omega \rightarrow \infty}$ . 713

684 Seven different finite fields were applied along each direction 714  
 685 ( $y, z$  and  $y = z$ ) in Lacivita et al. (2012), namely  $|\mathbf{E}| = 0.1,$  715  
 686  $0.5, 1, 2.5, 5, 7.5, 10 \times 10^{-3}$  a.u.. Overall, 21 field-dependent 716  
 687 geometry optimizations,  $\mathbf{R}_E$ , followed by the SC-CP1 calcu- 717  
 688 lations at the first order of perturbation were used to generate 718  
 689  $\boldsymbol{\mu}(\mathbf{R}_E), \boldsymbol{\alpha}^e(\mathbf{R}_E)$  (left hand side of Eq. 28) and  $\boldsymbol{\beta}^e(\mathbf{R}_E)$ . To 719  
 690 extract the nuclear relaxation (hyper)polarizabilities from the 720  
 691 Taylor expansions of the dipole moment and (hyper) 721  
 692 polarizabilities (right-hand side of Eqs. 29 and 30 for the 722  
 693 polarizability), an additional set of SC-CP2 calculations at the 723  
 694 second-order of perturbation was performed at the field- 724  
 695 free optimized geometry,  $\mathbf{R}_0$ . Total and nuclear relaxation 725  
 696 contributions to  $\boldsymbol{\gamma}$  are reported in Table 1. 726

697 Let us consider first the transverse (in-plane and non-peri- 727  
 698 odic)  $yyyy$ -component of  $\boldsymbol{\gamma}$ . The vibrational contribution 728  
 699 to the static value,  $\gamma_4^{nr}(0;0,0,0) = 1169$  a.u. for four static fields, 729  
 700 is almost 50% of the total value,  $g^{\mu}(0;0,0,0) = 2419$  a.u., 730  
 701 while this percentage decreases to 25% and  $-2\%$  when 731  
 702 only two or one fields are static,  $\gamma_2^{nr}(-\omega;\omega,0,0)$  and 732  
 703  $\gamma_4^{nr}(-2\omega;\omega,\omega,0)$ , respectively. The same comment applies 733  
 704 to components including the out-of-plane  $z$ -direction and 734  
 705 off-diagonal  $yz$  indices.

In the longitudinal  $x$ -direction of PA, no components of  $\boldsymbol{\gamma}$  can be calculated from the fit of the dipole moment with respect to static fields, since its  $\mu_x$ -component is ill-defined. Then, only components of  $\boldsymbol{\gamma}$  having 1, 2, or 3  $x$ -indices can be obtained from fits of  $\alpha_{xy(z)}^e$  and  $\beta_{xyz}^e, \alpha_{xx}^e$  and  $\beta_{xy(z)}^e$ , and  $\beta_{xxx}^e$  with respect to static  $E_y$  and  $E_z$  fields. This means that at least one field must be frequency-dependent, leading then to a small nuclear relaxation contribution  $\gamma_1^{nr}$  to  $g^\beta$  with respect to the electronic one. However, the vibrational contribution is larger than the electronic one for the two-static field  $g^\alpha$  non-linear optic property, particularly when both in-plane periodic  $x$  and non-periodic  $y$  components are involved. In the case of  $\gamma_{xyy}(-\omega;\omega,0,0)$ , the vibrational contribution,  $\gamma_2^{nr}$ , is equal to  $+2.332 \times 10^4$  a.u., while the total value is smaller:  $g^\alpha = +9877$  a.u., showing that the electronic contribution has an opposite sign with respect to the vibrational contribution, being equal to  $-1.334 \times 10^4$  a.u..

It is worth noting that  $\gamma_{xxx}^{nr}$  for the intensity-dependent refractive index (IDRI) process depends on the Raman intensities only, as  $\alpha_{xx}^{nr}$  depends on the IR intensities, and can be directly obtained as follows (Champagne et al. 1997):

$$\gamma_{xxx}^{nr}(-\omega;\omega,-\omega,\omega) = 2 \sum_{i=1}^{3N-6} \frac{\left(\frac{d\alpha_{xx}^e}{dQ_i}\right)^2}{\omega_i^2 - \omega^2}, \tag{32}$$

The CRYSTAL code computes the Raman intensities, and then allows to analytically obtain this parallel IDRI vibrational contribution too, which is of the same order of magnitude as the electronic one, around  $6 \times 10^6$  a.u. at the HF level of calculation with a 6-31G basis set including ghost atoms (basis set B in Lacivita et al. 2012).

**Table 1** FF-NR static and dynamic vibrational (nuclear relaxation) contributions to the second hyperpolarizability  $\boldsymbol{\gamma}$  (in a.u.) of PA obtained by fitting (a) the dipole moment, (b) the polarizability and (c) the first hyperpolarizability versus the finite field (according to Eq. 28 in the polarizability case)

	Fitted values					
	(a)		(b)		(c)	
	$g^\mu$	$\gamma_4^{nr}$	$g^\alpha$	$\gamma_2^{nr}$	$g^\beta$	$\gamma_1^{nr}$
yyyy	2419 ± 44	1169	1672 ± 26	422	1223 ± 8	-27
zzzz	2843 ± 283	371	2780 ± 16	308	2514 ± 6	42
xxxy	-	-	-	-	$(1.373 \pm 0.004) \times 10^5$	2900
xyyy	-	-	1675 ± 80	5247	-3614 ± 5	-42
xxyy	-	-	9877 ± 1009	$2.332 \times 10^4$	$(-1.358 \pm 0.002) \times 10^4$	-140
xxzz	-	-	$(1.158 \pm 0.241) \times 10^4$	5874	5766 ± 7	60
yyzz	1541 ± 17	933	861.3 ± 15.7	253.2	658.1 ± 3.1	50
zzyy	= yyzz	= yyzz	671.7 ± 7.3	63.7	602.6 ± 0.9	-5.5
zyyz	= yyzz	= yyzz	1855 ± 31	1247	= yyzz	= yyzz
xyzz	-	-	879.4 ± 202.8	659.5	250.2 ± 1.9	30.3
xzyz	-	-	2740 ± 86	2520	= xyzz	= xyzz
xzzy	-	-	= xzyz	= xzyz	220.0 ± 0.1	0.1

HF Hamiltonian and 6-31G(d) basis set including ghost atoms

735 The static  $\gamma_{xxxx}^{nr}(0;0,0,0)$  term, instead, needs also the  
 736 determination of the product of IR and hyper-Raman ampli-  
 737 tudes,  $(d\mu_x/dQ_i)(d\beta_{xxx}^e/dQ_i)$ , to be evaluated at the equilib-  
 738 rium geometry. The latter is not yet available in the CRYSTAL  
 739 code. Nevertheless, in the polyacetylene case, the IR  
 740 intensity is small, leading to  $\alpha_{xx}^{nr} \ll \alpha_{xx}^e$  [0.2 and 171.5 a.u.,  
 741 respectively (Lacivita et al. 2012)] and then most probably  
 742 to a small contribution, such that the very large  $\gamma_{xxxx}^{nr}(0;0,0,0)$   
 743 value can be evaluated from Eq. 32 with  $\omega = 0$ .

### 744 3.2 KDP and urea: dielectric tensor $\epsilon^e$ , 745 second-harmonic generation $d^e$ , and the effect 746 of the field wavelength $\lambda$

747 In the previous example of polyacetylene, the subscript  
 748  $\omega \rightarrow \infty$  in Eqs. 29 and 30 means that only the electronic  
 749 transitions, the energies of which are much larger than the  
 750 IR mode ones, are involved in the corresponding high-fre-  
 751 quency ("infinite frequency") electric field perturbation, but  
 752 the frequency was set to zero in the calculation. In the pre-  
 753 sent section, the effect of the field wavelength is studied on  
 754 the electronic contribution to the so-called high-frequency  
 755 or optical dielectric tensors.

756 Let us consider the examples of tetragonal KDP and urea.  
 757 In Table 2, the non-null components of the optical dielectric  
 758 tensor and SHG susceptibility (electronic contribution only,  
 759  $\epsilon^e$  and  $d^e$ ) at zero frequency, as obtained at the HF level  
 760 and with various DFT functionals, are reported, and com-  
 761 pared with the experimental determinations at  $\lambda = 1064$  nm  
 762 wavelength. The ionic contribution to electric properties at  
 763 this wavenumber is negligible, but the corresponding photon  
 764 energy ( $\sim 1$  eV) is by far smaller than the gap value (and  
 765 the UV-visible absorption edge), confirming that it can be  
 766 considered as null in the electronic contribution as we will  
 767 see further:  $\epsilon_{\lambda=1064nm}^{e+nr} \sim \epsilon_{\lambda \rightarrow \infty}^e$ .

768  $\epsilon$  is a symmetric second-order tensor; only two compo-  
 769 nents,  $\epsilon_{xx}$  and  $\epsilon_{zz}$ , are independent and non-null for sym-  
 770 metry reasons. As regards the third-rank SHG  $d = \frac{1}{2}\chi^{(2)}$ ,  
 771 only one non-equivalent component ( $xyz$ ) survives. It should

772 be underlined that *part* of the reduction of the number of  
 773 independent terms is due to the intrinsic symmetry of the  
 774 physical property (for  $\epsilon$ , its symmetric character reduces the  
 775 constants from 9 to 6; in a similar way, the intrinsic symme-  
 776 try of SHG reduces, for a triclinic compound, the non-null  
 777 and non-equivalent terms from 27 to 10). In the last line of  
 778 Table 2, the band gap is also reported, due to its relevance in  
 779 determining the numerical values of the various quantities.

780 Tables 2 and 3 permit to discuss two points characterizing  
 781 the simulation of the reported properties, and of the SC-CP  
 782 approach:

- 783 (a) the effect of the adopted functional;
- 784 (b) the effect of the self-consistent treatment.

785 As regards point (a), in the tables, the results obtained with  
 786 five of the most popular approaches, namely HF, LDA (Per-  
 787 dew and Zunger 1981), PBE (Perdew et al. 1996), PBE0  
 788 (Adamo and Barone 1999), and B3LYP (Becke 1993; Lee  
 789 et al. 1988), are reported. The HF Hamiltonian is known to  
 790 be affected by a universal overestimation of the band gap  
 791  $E_g$  (15.99 vs 7.12 eV, + 125%). This leads to a systematic  
 792 underestimation of the dielectric properties ( $-10\%$  for  $\epsilon_{xx}^e$ ,  
 793  $-49\%$  for  $d_{xyz}^e$ ): remember that CPHF and CPKS are SC-CP  
 794 perturbative schemes in which the gap appears in the denom-  
 795 inator in the analytical definition of the optical properties,  
 796 see, for example, Eq. 10 where  $\omega_n \geq \text{gap}$ .

797 At the other extreme, the LDA energy gap is underesti-  
 798 mated (5.72 vs 7.12 eV,  $-20\%$ ), because of the self-interac-  
 799 tion error; as a consequence, also the (hyper)polarizabilities  
 800 are generally overestimated (+ 4% for  $\epsilon_{xx}^e$ , + 25% for  $d_{xyz}^e$ ).

801 Gradient corrections (e.g., PBE) provide only small  
 802 improvements for the gap ( $-16\%$ ), and for the dielectric  
 803 properties (+ 4% for  $\epsilon_{xx}^e$ , + 20% for  $d_{xyz}^e$ ).

804 When the two hybrid functionals, B3LYP (+ 12% for  
 805 the gap) or PBE0 (+ 20%, about the same error, with oppo-  
 806 site sign, of LDA), are used, the difference with respect  
 807 to experiment is usually smaller than when using LDA  
 808 or PBE (0% for  $\epsilon_{xx}^e$ ,  $-4\%$  for  $d_{xyz}^e$  for B3LYP,  $-1\%$  for  $\epsilon_{xx}^e$ ,

**Table 2** Coupled-perturbed optical dielectric constants,  $\epsilon_{xx}^e$  and  $\epsilon_{zz}^e$ , and SHG susceptibility,  $d_{xyz}^e$  (in pm/V), of tetragonal KDP (space group I4d2) at zero frequency and different levels of theory

	HF	PBE0	B3LYP	PBE	LDA	Exp.
$\epsilon_{xx}^e$	2.025 (1.712)	2.223 (2.195)	2.230 (2.244)	2.328 (2.526)	2.340 (2.562)	2.23 <sup>a</sup>
$\epsilon_{zz}^e$	1.868 (1.639)	2.039 (2.043)	2.046 (2.086)	2.132 (2.317)	2.159 (2.369)	2.13 <sup>a</sup>
$d_{xyz}^e$	0.197 (0.066)	0.355 (0.302)	0.373 (0.341)	0.467 (0.609)	0.488 (0.647)	0.38 <sup>b</sup>
$E_g$	15.99	8.51	7.99	6.00	5.72	

A split valence basis set was used with d functions on H and f-functions on K, P, and O. SOS (sum over states) values in parentheses.  $E_g$  is the energy gap (in eV). Calculated data from Lacivita et al. (2009). Experimental values from <sup>a</sup> Polyanskiy (2020) and <sup>b</sup> Eckardt and Byer (1991) at  $\lambda = 1064$  nm



**Table 3** High-frequency dielectric tensor components  $\epsilon_{xx}^e$  and  $\epsilon_{zz}^e$  of urea (three top lines) and KDP (three bottom lines) computed using various Hamiltonians at  $\lambda \rightarrow \infty$  limit and  $\lambda$  equal to 1064 and 600 nm

	$\lambda$ (nm)		HF	PBE0	B3LYP	LC-BLYP	PBE	LDA	Exp.
Urea	$\infty$	$\epsilon_{xx}^e$	1.901	2.059	2.070	2.057	2.149	2.186	
		$\epsilon_{zz}^e$	2.187	2.433	2.451	2.430	2.567	2.599	
	1064	$\epsilon_{xx}^e$	1.907	2.070	2.081	2.067	2.163	2.202	2.194
		$\epsilon_{zz}^e$	2.195	2.448	2.467	2.446	2.588	2.621	2.529
	600	$\epsilon_{xx}^e$	1.920	2.093	2.106	2.091	2.195	2.237	2.220
		$\epsilon_{zz}^e$	2.214	2.483	2.504	2.481	2.635	2.671	2.577
KDP	$\infty$	$\epsilon_{xx}^e$	2.025	2.223	2.230	2.219	2.327	2.341	
		$\epsilon_{zz}^e$	1.868	2.039	2.046	2.049	2.132	2.160	
	1064	$\epsilon_{xx}^e$	2.030	2.231	2.239	2.227	2.339	2.352	2.231
		$\epsilon_{zz}^e$	1.872	2.046	2.053	2.055	2.141	2.169	2.131
	600	$\epsilon_{xx}^e$	2.041	2.250	2.258	2.245	2.363	2.377	2.277
		$\epsilon_{zz}^e$	1.880	2.060	2.068	2.069	2.160	2.189	2.155

Data from Rérat et al. (2015). Experimental values from Rosker et al. (1985) for urea and Polyanskiy (2020) for KDP

809  $-8\%$  for  $d_{xyz}^e$  for PBE0). Note, however, that if the other  
810 component of the dielectric tensor is considered,  $\epsilon_{zz}^e$ , the  
811 LDA or PBE results are closer to experiment than the ones  
812 of hybrids (+ 1%, 0%,  $-4\%$ ,  $-4\%$  and  $-12\%$ , from left to  
813 right in the table).

814 Let us consider now the effect of the SCF process, which  
815 permits to the system to respond to the electric field pertur-  
816 bation [point (b) above]. The self-consistent coupled-per-  
817 turbed, SC-CP, results can be compared with the uncoupled  
818 SOS (sum over states; iteration 0 of the SC-CP process) data  
819 shown in parentheses in any second row of the table.

820 A few comments concerning  $\epsilon^e$ :

- 821 – In all cases, the coupled-perturbed scheme improves the
- 822 SOS results.
- 823 – The larger the distance  $\Delta$  from the experiment at the SOS
- 824 level, the larger the SC-CP correction (SC-CP minus
- 825 SOS): for HF,  $\epsilon_{xx}^e$  varies by 0.32 (from 1.71 to 2.03) and
- 826  $\Delta$  from  $-24$  to  $-10\%$ ; for LDA, at the opposite side of the
- 827 table,  $\epsilon_{xx}^e$  decreases from 2.56 to 2.34 and  $\Delta$  from + 14 to
- 828 + 4%.

829 It is interesting to notice that for hybrids, and in particular  
830 for B3LYP, the difference between SOS and SC-CP is quite  
831 small (0.01 and 0.04 for  $\epsilon_{xx}^e$  and  $\epsilon_{zz}^e$  for B3LYP, and 0.03  
832 and 0.00 for PBE0 for the same components, with  $\Delta$  always  
833 smaller than 4%). In summary, hybrid functionals seem to  
834 require a much smaller correction from the coupling than  
835 LDA, PBE, and HF.

836 The above comments apply also to the SHG  $d_{xyz}^e$  data;  
837 the effects are, however, much larger in percentage. There-  
838 fore, for HF,  $\Delta$  increases from  $-83\%$  to  $-49\%$ ; for LDA, it  
839 decreases from + 66 to + 25%; for B3LYP from  $-13$  to  $-4\%$ ,  
840 with a relatively modest change in absolute value from 0.34  
841 to 0.37 pm/V.

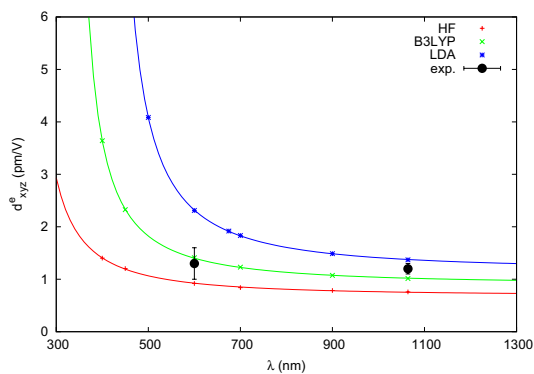
The data shown in Table 2 are static, but they refer to elec-  
tronic calculations or measurements in which a high (UV–vis-  
ible) field frequency has been used. In Table 3, we explore, for  
both urea and KDP, the effect of the field wavelength, for the  
electronic dielectric tensor (Rérat et al. 2015). Computed SHG  
results for urea and KDP (see Table 4) show that B3LYP  
reproduces rather well the experimental values measured at  
1064 and 600 nm. For urea, the quasi-isotropic electronic con-  
tribution is slightly smaller than the experimental value at  
 $\lambda = 1064$  nm (Halbout et al. 1979). At this wavelength, the  
vibrational contribution may not be completely negligible. For  
that reason, the double harmonic vibrational  $d_{xyz(zxy)}^{nr}(-2\omega; \omega, \omega)$   
components were calculated at  $\lambda = 1064$  nm (see Eq. 6 in  
Rérat et al. 2015); their value is 0.041 (0.035) pm V<sup>-1</sup> for  
B3LYP, and has the same sign as the electronic contribution  
 $d_{xyz(zxy)}^e(-2\omega; \omega, \omega)$ . The total B3LYP  $d_{xyz(zxy)}^{e+nr}$  value is, then,  
equal to 1.027 and 1.018 pm V<sup>-1</sup> which falls essentially at the  
outer limit of the error bars for the experimental value:  
 $d_{14} = 1.2 \pm 0.1$  pm V<sup>-1</sup> of Halbout et al. (1979) ( $d_{xyz}^{e+nr} \approx d_{xyz}^e$   
for wavelength larger than 600 nm). Vibrational anharmonicity  
and/or temperature effects, which would increase the magni-  
tude of this term, could be among the reasons of the small  
discrepancy. At 600 nm, the calculated vibrational contribution  
is four times smaller than at 1064 nm and, thus, can be  
neglected. The B3LYP value (1.371 and 1.361 pm V<sup>-1</sup>) in this  
case is well within the experimental window:  $1.3 \pm 0.3$  pm V<sup>-1</sup>  
of Bäuerle et al. (1977). Finally, for KDP, the B3LYP elec-  
tronic value of 0.41 pm V<sup>-1</sup> is in perfect agreement with the  
available experimental reference, i.e., 0.41 pm V<sup>-1</sup> (Singh  
1986). Again, Table 4 clearly shows the well-known tendency  
of LDA and GGA functionals to grossly overestimate high-  
order electric susceptibilities as the value of the wavelength  
approaches the resonance. It is noteworthy that  $d_{xyz}^e$  increases  
at each frequency when the percentage of HF exchange



**Table 4** Calculated SHG high-frequency electric susceptibilities  $d_{xyz}^e$  and  $d_{zxy}^e$  (in pm/V) of urea and KDP computed using various Hamiltonians at  $\lambda \rightarrow \infty$  limit and  $\lambda$  equal to 1064 and 600 nm

	$\lambda$ (nm)		HF	PBE0	B3LYP	LC-BLYP	PBE	LDA	Exp.
Urea	$\infty$	$d_{xyz}^e$	0.680	0.823	0.863	0.876	0.949	1.106	
		$d_{zxy}^e$	0.680	0.823	0.863	0.876	0.949	1.106	
	1064	$d_{xyz}^e$	0.738	0.936	0.986	0.989	1.131	1.333	1.2±0.1
		$d_{zxy}^e$	0.737	0.934	0.983	0.988	1.128	1.329	
	600	$d_{xyz}^e$	0.894	1.279	1.371	1.333	1.824	2.243	1.3±0.3
		$d_{zxy}^e$	0.889	1.263	1.361	1.323	1.793	2.191	
KDP	$\infty$	$d_{xyz}^e$	0.198	0.354	0.373	0.342	0.467	0.487	
		$d_{zxy}^e$	0.198	0.354	0.373	0.342	0.467	0.487	
	1064	$d_{xyz}^e$	0.207	0.378	0.397	0.363	0.505	0.530	0.38, 0.41
		$d_{zxy}^e$	0.207	0.378	0.396	0.363	0.504	0.529	
	600	$d_{xyz}^e$	0.228	0.438	0.464	0.416	0.607	0.642	
		$d_{zxy}^e$	0.227	0.435	0.460	0.415	0.603	0.636	

Data as in Rérat et al. (2015). Experimental data from Levine and Allan (1993), Halbout et al. (1979), Bäuerle et al. (1977) for urea and from Refs. Eckardt and Byer (1991), Singh (1986) for KDP



**Fig. 2** Variation of the SHG  $d_{xyz}^e$  tensor component of bulk urea with respect to the field wavelength,  $\lambda$ , at the HF, B3LYP, and LDA levels of calculation. Experimental data from Levine and Allan (1993), Halbout et al. (1979), Bäuerle et al. (1977)

876 decreases. This correlates with the predicted band gap for the  
877 different Hamiltonians. For urea,  $E_g$  decreases from HF (14.0  
878 eV) to PBE0 (7.4 eV) and B3LYP (6.9 eV) to PBE (5.2 eV)  
879 and LDA (4.8 eV); see Table 2 for KDP.

880 Figure 2 shows the variation of SHG  $d_{xyz}^e$  as a function of  $\lambda$ ,  
881 the field wavelength, for three levels of theory: HF, LDA, and  
882 B3LYP. The dots represent the experimental determination.  
883 Its error bar is also indicated. The above discussion concern-  
884 ing the  $\lambda$  effect becomes here very clear: above 600 (HF), 700  
885 (B3LYP), or 1100 (LDA) nm  $d_{xyz}^e$  remains essentially constant  
886 when the wavelength of the field is varying. As for other prop-  
887 erties, B3LYP performs best.

### 3.3 Refractive index $n$ and birefringence $\delta$ of minerals

888  
889

The refractive index and birefringence are directly related by  
simple equations to the components of the dielectric tensor,  
as shown in Sect. 2.2.

Here, we will focus on three aspects:

890  
891  
892  
893

- 894 the relative importance of the electronic and ionic con-  
895 tributions. We remind that the former requires a CPHF  
896 calculation at fixed geometry (experimental or calcu-  
897 lated); the ionic contribution is more expensive, as it  
898 requires to build the full Hessian matrix for generating  
899 the vibrational frequencies.
- 900 the dependence of these contributions on the wave-  
901 length  $\lambda$
- 902 the *anisotropy*, that is the different response to the elec-  
903 tric field applied in different directions.

As discussed previously, the relative importance of the elec-  
tronic  $\alpha^e$  (Eq. 10) and ionic  $\alpha^{ion}$  (Eq. 12) contributions to  
polarizability depends on the frequency. In the UV–visible  
region, the electronic contribution is much larger than the  
ionic one. Therefore, we will first consider results obtained  
at the sodium source wavelength,  $\lambda_D = 589.3$  nm, taking into  
account the electronic contribution alone.

904  
905  
906  
907  
908  
909  
910

A large set of minerals, namely fluorite ( $\text{CaF}_2$ ), periclase  
( $\text{MgO}$ ), corundum ( $\text{Al}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ), rutile ( $\text{TiO}_2$ ),  
anatase ( $\text{TiO}_2$ ), calcite ( $\text{CaCO}_3$ ), aragonite ( $\text{CaCO}_3$ ), anda-  
lusite, sillimanite, and kyanite (three  $\text{Al}_2\text{SiO}_5$  polymorphs),  
forsterite ( $\text{Mg}_2\text{SiO}_4$ ), topaz ( $\text{Al}_2\text{SiO}_4\text{F}_2$ ), and perovskite  
( $\text{CaTiO}_3$ ), plus CaO have been selected to cover a large  
range of refractive index and birefringence values. Table 5  
reports data calculated for this set of systems, using the  
B3LYP hybrid functional, relatively severe computational

911  
912  
913  
914  
915  
916  
917  
918  
919

**Table 5** Calculated and experimental refractive indices both at ( $\lambda_D$ ) for various minerals characterized by different symmetry

MI	CS	Experimental data					Calculated data				
		$n_x$	$n_y$	$n_z$	$\delta$	$2V_z$	$n_x$	$n_y$	$n_z$	$\delta$	$2V_z$
Flu	Cub		1.4336					1.4325			
Per	Cub		1.7355					1.7249			
CaO	Cub		1.8396					1.8205			
Cor	Trig	1.7598		1.7673	-.0085		1.7326		1.7442	-.0117	
Qtz	Trig		1.5441	1.553	+.0090			1.5304	1.5365	+.0061	
Ru	Tet		2.613	2.900	+.287			2.5773	2.8447	+.2674	
Ana	Tet	2.4889		2.5621	-.0732		2.4189		2.5147	-.0958	
Cal	Rho	1.486		1.658	-.172		1.4796		1.6393	-.1597	
Ara	Ort	1.530	1.681	1.685	-.155	162.0	1.5245	1.6754	1.6805	-.1560	160.7
And	Ort	1.6327	1.6387	1.6439	-.0112	94.4	1.6180	1.6254	1.6287	-.0107	112.8
Sil	Ort	1.6576	1.6592	1.6797	+.0221	31.5	1.6378	1.6389	1.6557	+.0179	28.5
Ky	Tric	1.7130	1.7221	1.7287	-.0157	99.5	1.7029	1.7114	1.7181	-.0152	97.3
Fo	Ort	1.6358	1.6506	1.6687	+.0329	85.1	1.6112	1.6256	1.6472	+.0360	79.4
Top	Ort	1.6107	1.6136	1.6209	+.0102	66.7	1.5920	1.5956	1.5986	-.0066	95.1
Top	Ort						1.5920	1.5944	1.5998	+.0078	66.6
Pv	Ort	nd	nd	nd	0.018*	nd	2.3440	2.3497	2.3631	+.0191	66.7
Pv	Ort						2.3492	2.3529	2.3790	+.0298	42.0

For each mineral (col. 1: Flu: Fluorite, Per: Periclase, CaO, Cor: corundum, Qtz: quartz, Ru: rutile, Ana: anatase, Cal: calcite, Ara: aragonite, And: andalusite, Sil: sillimanite, Ky: kyanite, Fo: forsterite, Top: topaz, Pv: perovskite) the crystalline system is reported (col. 2: Cub: cubic, Tet: tetragonal, Trig: trigonal, Rho: rhomboedrical, Ort: orthorhombic, Tric: triclinic). Columns 3–5, 6, and 7 report the experimental refractive indices, the birefringence, and the  $2V_z$  angle, respectively. The corresponding calculated values are given in columns 8–10, 11, and 12, respectively. The sign associated with the birefringence  $\delta$  is the optical sign. For uniaxial crystals,  $n_y = n_\omega$  and  $n_z = n_e$  for the positive ones and  $n_x = n_e$  and  $n_z = n_\omega$  for the negative ones.  $2V_z$  is smaller (larger) than 90 degrees for positive (negative) biaxial compounds. Opening braces indicate sets of polymorphs. Experimental refractive indices from the compilation at Shannon et al. (2002); when several data are available, preference has been given to data agreeing with Fleischer et al. (1984). The accuracy on the refractive experimental indices is  $\pm(0.0001 - 0.0010)$ . The variations between different measurements are usually of the order of 0.001. Opening parentheses associate calculations performed at the experimental (first line) and optimized (second line) geometry

\*See text about birefringence of perovskite

920 conditions, and the basis sets developed by Peintinger et al. 948  
 921 (2013). In all but two cases, the experimental geometry has 949  
 922 been used. The refractive indices obtained at the optimized 950  
 923 geometry are extremely close to the ones computed at the 951  
 924 experimental geometry, the exceptions being topaz and 952  
 925 perovskite, for which both data are reported in the table. 953  
 926 Figure 3 shows the birefringence ( $\delta$ ) as a function of the 954  
 927 refringence expressed by the proxy  $\tilde{n}$ . In general, being the 955  
 928 birefringence a small fraction of the refractive indices, the 956  
 929 intermediate refractive index is a good approximation of 957  
 930 the refringence. Therefore,  $\tilde{n} = n_y$ ,  $\tilde{n} = n_\omega$ , and  $\tilde{n} = n$  for 958  
 931 biaxial, uniaxial, and cubic crystals, respectively.

932 Consider first the cubic systems, on the zero axis. For 959  
 933 fluorite and CaO, simulation and experiment coincide, 960  
 934 whereas, for periclase, the experimental value is slightly 961  
 935 larger (1.735 vs 1.725). This is always the case for all sys- 962  
 936 tems: when the two circles do not overlap, the experimental 963  
 937  $\tilde{n}$  value is always slightly larger than the computed one, the 964  
 938 difference being of the order of 2–3%.

939 Three sets of polymorphs have been considered: (rutile, 965  
 940 anatase), (calcite, aragonite), and (andalusite, sillimanite, 966  
 941 kyanite). As already observed for the andradite-grossular 967  
 942 solid solution (Lacivita et al. 2013), polymorphs with close 968  
 943 density (for example, andalusite, sillimanite) present similar 969  
 944 indices. When the density is different, the denser system 970  
 945 has the largest  $\tilde{n}$  value, as is the case of anatase-rutile and 971  
 946 of andalusite–kyanite, according to the Gladstone–Dale or 972  
 947 Drude law (Anderson and Schreiber 1965). In summary, the 973  
 974  
 975

$\tilde{n}$  experimental data are well reproduced, and the residual 948  
 error is small, and always with the same sign. 949

950 The agreement between the experimental and calculated 951  
 952 birefringence (the difference between the smallest and larg- 953  
 954 est refractive indices) is better than the one for  $\tilde{n}$  by about 955  
 956 one order of magnitude. This is due to the fact that inac- 957  
 958 curacies due to basis set limitations, use of a specific func- 959  
 960 tional, definition of the equilibrium geometry, and numerical 961  
 962 approximations are to a large amount the same for the dif- 963  
 964 ferent components of the dielectric tensor, and then cancel 964  
 965 when computing birefringence. 965  
 966

967 The comparison of calculated and experimental optical 968  
 969 sign and angle is more delicate. Figure 3 confirms that for 969  
 970 uniaxial crystals, the optical sign is correctly predicted, also 970  
 971 for quartz or corundum which are characterized by a small 971  
 972 birefringence. For corundum, the discrepancy is the largest 972  
 973 in the set; note, however, that the experimental birefringence 973  
 974 is the smallest in the set. This indicates that the evaluation 974  
 975 of the optical sign of weakly birefringent uniaxial crystals 975  
 is delicate.

968 For the biaxial crystals, the optical sign and angle are 968  
 969 connected. In general, the agreement between calculated 969  
 970 and experimental optical signs is good. A closer inspection 970  
 971 reveals, however, the difficulty of obtaining the precise shape 971  
 972 of the indicatrix, as the interesting case of topaz, orthorhombic, 972  
 973 shows. The "module" of the calculated birefringence 973  
 974 compares satisfactorily to the experimental one (0.0102) 974  
 975 either at the experimental (0.0066) or optimized (0.0078) 975



**Fig. 3** Birefringence ( $\delta$ ) versus refringence ( $\tilde{n}$ ). See text for the definition of  $\tilde{n}$ , that depends on the crystalline system. Positive and negative uniaxial or biaxial minerals are reported in the upper (blue circles) and lower (red circles) part of the figure, respectively. Open and closed circles correspond to calculated and experimental values, respectively. The ellipse corresponds to perovskite and is centered on the reported interval of indices and the largest measured birefringence (see text); the optical sign is unknown. Abbreviations are as follows: Flu: fluorite, Per: periclase, Cor: corundum, Ru: rutile, Ana: anatase, Cal: calcite, Ara: aragonite, Fo: forsterite, And: andalusite, Sil: sillimanite, Ky: kyanite, Qtz: quartz, Top: topaz, Pv: perovskite. When circles overlap, in all cases, they refer to the same compound, that is indicated only in one of the circles

976 geometry. However, the sign of the calculated indicatrix  
977 reverses according to the considered geometry.

978 We mention here also the  $\text{CaTiO}_3$  perovskite case, whose  
979 crystals are finely twinned. We are not aware of any experi-  
980 mental determination of the refractive indices, as Table 5  
981 shows. We found, however, a single experimental determina-  
982 tion of the birefringence (El-mallah et al. 1987). We indicate  
983 this situation with an ellipse, rather than with a circle. The  $\delta$   
984 value computed at the experimental geometry is quite close  
985 to the experimental value (0.019 vs 0.018), whereas the  
986 value at the optimized geometry is slightly larger (0.030).

987 A few words now concern the optical angle  $2V$ , shown  
988 in Table 5, for which we consider again topaz and perovs-  
989 kite. In both cases, the calculated refractive indices at the  
990 two geometries are quite close, but the optical angles are  
991 different, and strongly dependent on these small differ-  
992 ences. The reason is that the size of the indicatrix depends  
993 on the refractive index values, whereas the shape is mainly

**Table 6** Comparison between calculated and measured refractive indices  $n_{\lambda_D}$  and  $n_{\lambda_{\max}}$

MI	$\lambda_D$		$\lambda_{\max}$		$\lambda_{\max}$
	Calc.	Exp.	Calc.	Exp.	
Flu	1.4325	1.4336	1.3001	1.3076	9724.0 <sup>a</sup>
Cor	1.7442 <sup>o</sup>	1.7673	1.5597	1.5864	5577.0 <sup>b</sup>
	1.7326 <sup>e</sup>	1.7598	1.5541 <sup>e</sup>		
Per	1.7249	1.7355	1.6100	1.6240	5350.0 <sup>c</sup>
Cal	1.6392 <sup>o</sup>	1.658	1.6057	1.6210	2170.0 <sup>d</sup>
	1.4796 <sup>e</sup>	1.486	1.4656	1.4739	
Qtz	1.5304 <sup>o</sup>	1.5441	1.5027	1.5201	2053.1 <sup>d</sup>
	1.5365 <sup>e</sup>	1.553	1.5103	1.5282	
Ru	2.5773 <sup>o</sup>	2.613	2.4112	2.451	1529.6 <sup>e</sup>
	2.8447 <sup>e</sup>	2.900	2.6501	2.709	

$\lambda_{\max}$  in nm in the last column. For uniaxial minerals, superscripts *o* and *e* underline that the lines report  $n_o$  and  $n_e$ , respectively

<sup>a</sup>Malitson (1963)

<sup>b</sup>Malitson (1962)

<sup>c</sup>Stephens and Malitson (1952)

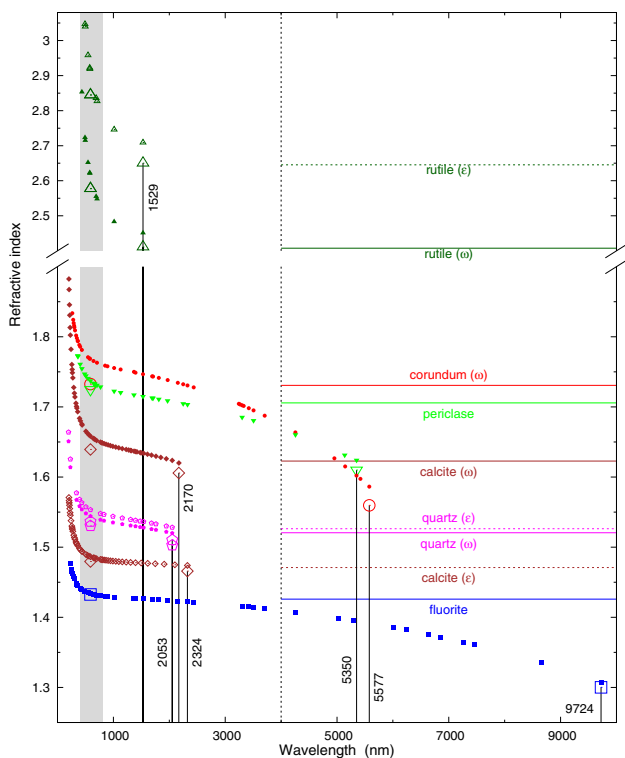
<sup>d</sup>Ghosh (1999)

<sup>e</sup>Devore (1951)

controlled by the two partial birefringences:  $\delta_1 = n_Y - n_X$  994  
and  $\delta_2 = n_Z - n_Y$ . Note that  $\delta = \delta_1 + \delta_2$  (Wright 1951). For 995  
 $\delta < 0.05$  and  $1.400 < n_X < 2.000$ , the main contribution to 996  
 $\cos 2V_Z$  is given by  $\frac{\delta_2 - \delta_1}{\delta}$ . The partial birefringence being 997  
smaller than the birefringence, small changes of the partial 998  
birefringence can change the optical sign. Therefore, at this 999  
stage, the calculated sign of the indicatrix of biaxial materi- 1000  
als has to be considered as poorly constrained. 1001

As anticipated, at wavelengths shorter than the IR region, 1002  
the polarizability, and, consequently, the dielectric matrix 1003  
(Eq. 26) and refractive index (Eq. 16), can be approximated 1004  
by its electronic part only, since  $\alpha^{nr} \sim -\sum_i \sigma_i^2 / \omega^2 \sim 0^-$  (see 1005  
Eq. 12 with  $\omega \gg \omega_i$ ). However, defining a precise limit for 1006  
IR is not simple. It depends on the frequency modes ( $\omega_i$ ) and 1007  
corresponding Born charges ( $\sigma_i$ ) of the considered systems. 1008  
Practically, 4000 nm (equivalent to  $2500 \text{ cm}^{-1}$ ) is a provi- 1009  
sional limit that should be applied to most of the studied sys- 1010  
tems. Hence, experimental indices measured at wavelength 1011  
shorter than about 4000 nm should be larger than refractive 1012  
indices evaluated at infinity, when considering only the elec- 1013  
tronic part ( $n_{\lambda \rightarrow \infty}^e$ ), since  $\alpha^e = \sum_n f_n / (\omega_n^2 - \omega^2)$  (see Eq. 10) 1014  
increases with respect to  $\omega$  till the first resonance  $\omega = \omega_n$  in 1015  
the UV-visible spectrum ( $\lambda < 600 \text{ nm}$ ) for many minerals. 1016

Then, we have performed a literature search to find 1017  
experimental dispersion of the refractive index with 1018  
respect to the photon energy between the IR and UV-visible 1019  
absorption spectra ( $\lambda \in [200 - 10,000] \text{ nm}$ ). Available 1020  
data are represented in Fig. 4. Table 6 reports the larg- 1021  
est wavelength ( $\lambda_{\max}$ ) at which the refractive index of the 1022



**Fig. 4** Refractive index as function of wavelength. Large and small symbols correspond to calculated and measured indices, respectively. Square, circle, downward triangle, upward triangle, diamond, and pentagon correspond to fluorite, corundum, periclase, rutile, calcite, and quartz, respectively. Empty large symbols within and outside the vertical grey strip indicate  $n_{\lambda_D}$  and  $n_{\lambda_{max}}^{e+nr}$ , respectively. The horizontal lines at height  $n_{\lambda \rightarrow \infty}^e$  allow to appreciate the role of the ionic contribution to refractive index. For uniaxial crystals, solid and dashed lines refer to  $n_\omega$  and  $n_e$ , respectively.  $\lambda_{max}$  is indicated along the vertical line (see Table 6). Color refers to the compound. The grey strip indicates the visible region. The vertical scale of the upper part is half that of the lower part. Notice that no dispersion data have been found for  $n_e$  of corundum

1023 considered materials have been measured, and the cor-  
 1024 responding measured indices ( $n_{\lambda_{max}}$ ), as well as  $n_{\lambda_D}$ , cor-  
 1025 responding to the yellow line of Na. For quartz, calcite  
 1026 and rutile,  $\lambda_{max}$  is in the near IR and significantly shorter  
 1027 than 4000 nm. For the first two systems,  $n_{\lambda_{max}}$  is close to  
 1028 the  $n_{\lambda \rightarrow \infty}^e$  limit value represented by horizontal lines in  
 1029 Fig. 4. For rutile, whose  $\lambda_{max}$  is close to the visible spec-  
 1030 trum represented by the vertical grey strip,  $n_{\lambda_{max}}$  is smaller  
 1031 than  $n_{\lambda \rightarrow \infty}^e$ . The difference  $n_{\lambda \rightarrow \infty}^e - n_{\lambda_{max}}$  is comparable to  
 1032 its equivalent at  $\lambda_D$ . For fluorite, corundum, and periclase,  
 1033  $\lambda_{max}$  largely exceeds 4000 nm and the  $n_{\lambda_{max}}$  values are much  
 1034 smaller than  $n_{\lambda \rightarrow \infty}^e$ , due to the negative ionic contribu-  
 1035 tion, see Eq. 12 when  $\omega > \omega_i$ . The larger  $n_{\lambda_{max}}$ , the larger  
 1036  $n_{\lambda \rightarrow \infty}^e - n_{\lambda_{max}}$  (Fig. 4). The difference reaches almost 10%  
 1037 in the cases of corundum and fluorite and the electronic  
 1038 polarizability alone fails to reproduce indices measured at  
 1039 large wavelengths.

1040 Frequency calculations were performed to evaluate  $\alpha^{nr}(\omega)$   
 1041 (Eq. 12) and the polarizability was evaluated considering the  
 1042 two contributions. In the case of fluorite, corundum and  
 1043 periclase, including the ionic contribution, yield calculated  
 1044 refractive indices ( $n_{\lambda_{max}}^{e+nr}$ ) in very good agreement with the  
 1045 experimental values (Table 6). The difference between calcu-  
 1046 lated and measured indices is now of the order of the dif-  
 1047 ference at  $\lambda_D$ . For rutile, calcite, and quartz, addition of the  
 1048 ionic contribution slightly reduces the calculated indices as  
 1049 expected.

1050 The relative  $\alpha^e$  and  $\alpha^{e+nr}$  contributions to the refractive  
 1051 index in the various spectral regions can be appreciated from  
 1052 Fig. 4 where experimental dispersion data and calculated  
 1053  $n_{\lambda_D}$ ,  $n_{\lambda \rightarrow \infty}^e$  and  $n_{\lambda_{max}}^{e+nr}$  are reported for the materials considered.  
 1054 As anticipated above, the electronic contribution yields a  
 1055 fairly good value of the index  $n_{\lambda_D}$  (large open symbols in the  
 1056 grey vertical strip). However,  $n_{\lambda \rightarrow \infty}^e$  (horizontal lines) deviate  
 1057 significantly from indices measured at  $\lambda > 4000$  nm. In fact,  
 1058 this "limit" depends on materials. From our data, a better  
 1059 provisional "limit" should be 2500 nm. Above 4000 (or  
 1060 2500) nm, the ionic contribution cannot be neglected and  
 1061 brings the calculated indices ( $n_{\lambda_{max}}^{e+nr}$ ) in very good agreement  
 1062 with experimental indices.

## 4 Conclusions

1063 In this document, it has been shown that ab initio quantum  
 1064 mechanical simulation can be used for the calculation of  
 1065 a large set of properties related to the perturbation of an  
 1066 electric field on a crystalline system. The simplest ones,  
 1067 like the dielectric tensor, the refractive indices, the birefrin-  
 1068 gence, correspond to the second order terms in the Taylor  
 1069 expansion of the total energy of the system as a function  
 1070 of the field strength. The laser technology permits now-  
 1071 days to access experimentally also to the third- and fourth-  
 1072 order terms in the expansion. The combination in various  
 1073 ways of the frequencies of the involved fields multiplies  
 1074 the number of phenomena and physical features that can  
 1075 be accessed experimentally. A large set of these (first and  
 1076 second hyperpolarizability, second-harmonic generation,  
 1077 intensity-dependent refractive indices, and many others) can  
 1078 be obtained from the CRYSTAL code used here, at rela-  
 1079 tively low cost for small-medium-size periodic systems (the  
 1080 most interesting, due to the tensor nature of many of these  
 1081 quantities).

1082 One of the big advantages of simulation is that the full set  
 1083 of constants defining the tensor are obtained with a single  
 1084 calculation, whereas many experiments must be performed  
 1085 for obtaining the same result.

1086 The combination with other perturbations, for example  
 1087 the strain of the unit cell, generates a new set of important  
 1088



1089 properties, like the piezoelectric (third order) or photoelastic  
1090 (fourth order) tensor, available as well in a very simple way  
1091 from CRYSTAL.

1092 Quantum mechanical simulation appears then an essential  
1093 tool for the accurate exploration of many tensorial properties  
1094 of crystalline compounds.

1095 **Acknowledgements** Access to the HPC resources of CINES/IDRIS/  
1096 TGCC obtained thanks to the Grants 2018-[A0040810471] (Fabien  
1097 Pascale) and 2018-[A0050810537] (Philippe D'Arco) made by GENCI  
1098 are warmly acknowledged. High-Performance Computing resources  
1099 were partially provided by the EXPLOR centre hosted by the Uni-  
1100 versity de Lorraine. This project has received funding from the ANR  
1101 (Agence Nationale de la Recherche)–FOIST (project number 18-CE24-  
1102 0030-03). Part of this work was granted access to the HPC resources of  
1103 [CCRT/CINES/IDRIS] under the allocation 2018–2019 and 2019–2020  
1104 [A0040807031] made by GENCI (Grand Equipement National de Cal-  
1105 cul Intensif). We also acknowledge the Direction du Numérique de  
1106 l'Université de Pau et des Pays de l'Adour for the computing facilities  
1107 provided.

## 1108 References

1109 Adamo C, Barone V (1999) Toward reliable density functional methods  
1110 without adjustable parameters: the PBE0 model. *J Chem Phys*  
1111 110(13):6158–6170. <https://doi.org/10.1063/1.478522>  
1112 Anderson OL, Schreiber E (1965) The relation between refractive index  
1113 and density of minerals related to the Earth's mantle. *J Geophys*  
1114 *Res* 70:1463–1471. <https://doi.org/10.1029/JZ070i006p01463>  
1115 Bäuerle D, Betzler K, Hesse H, Kapphan S, Loose P (1977) Phase-  
1116 matched second harmonic generation in urea. *Phys Status Solidi*  
1117 A 42(2):K119–K121. <https://doi.org/10.1002/pssa.2210420254>  
1118 Becke AD (1993) Density-functional thermochemistry. III. The role  
1119 of exact exchange. *J Chem Phys* 98(7):5648–5652. <https://doi.org/10.1063/1.464913>  
1120 Bishop DM (1999) Polarizability and hyperpolarizability of atoms and  
1121 ions. In: *Theoretical and computational chemistry*. Elsevier, pp  
1122 129–146. [https://doi.org/10.1016/s1380-7323\(99\)80007-7](https://doi.org/10.1016/s1380-7323(99)80007-7)  
1123 Bishop DM, Hasan M, Kirtman B (1995) A simple method for deter-  
1124 mining approximate static and dynamic vibrational hyperpolar-  
1125 izabilities. *J Chem Phys* 103(10):4157–4159. <https://doi.org/10.1063/1.469600>  
1126 Blount EI, Ehrenreich H, Seitz F, Turnbull D (1962) *Solid state phys-*  
1127 *ics*, vol 13. Academic, New York  
1128 Boulon G (2001) *Nonlinear optics: molecular engineering*. ScienceDi-  
1129 rect. <https://doi.org/10.1016/B0-08-043152-6/01111-6>  
1130 Boyd RW (2003) *Nonlinear optics*. Chapter 4: the intensity-dependent  
1131 refractive index. Elsevier. <https://doi.org/10.1016/B978-012121682-5/50005-5>  
1132 Champagne B, Perpète EA, André JM, Kirtman B (1997) Analysis of  
1133 the vibrational static and dynamic second hyperpolarizabilities  
1134 of polyacetylene chains. *Synth Met* 85:1047–1050. [https://doi.org/10.1016/S0379-6779\(97\)80146-4](https://doi.org/10.1016/S0379-6779(97)80146-4)  
1135 Condon EU (1937) Theories of optical rotatory power. *Rev Mod Phys*  
1136 9(4):432–457. <https://doi.org/10.1103/revmodphys.9.432>  
1137 Coulson CA (1941) II.—the Van der Waals force between a proton  
1138 and a hydrogen atom. *Proc R Soc Edinb Sect A Math Phys Sci*  
1139 61(1):20–25. <https://doi.org/10.1017/s0080454100006038>  
1140 Darrigan C, Rérat M, Mallia G, Dovesi R (2003) Implementation of the  
1141 finite field perturbation method in the crystal program for calculat-  
1142 ing the dielectric constant of periodic systems. *J Comput Chem*  
1143 24(11):1305–1312. <https://doi.org/10.1002/jcc.10274>

Devore JR (1951) Refractive indices of rutile and sphalerite. *J Opt Soc Am* 41(6):416–419. <https://doi.org/10.1364/JOSA.41.000416> 1148  
Dovesi R, Saunders VR, Roetti C, Orlando R, Zicovich-Wilson CM, 1149  
Pascale F, Civalleri B, Doll K, Harrison NM, Bush IJ, D'Arco 1150  
P, Llunell M, Causà M, Noël Y, Maschio L, Erba A, Rérat M, 1151  
Casassa S (2017) *Crystal17 User's Manual*. University of Torino. 1152  
<http://www.crystal.unito.it> 1153  
Dovesi R, Erba A, Orlando R, Zicovich-Wilson CM, Civalleri B, 1154  
Maschio L, Rérat M, Casassa S, Baima J, Salustro S, Kirtman B 1155  
(2018) Quantum-mechanical condensed matter simulations with 1156  
CRYSTAL. *Wiley Interdiscip Rev Comput Mol Sci* 8(4):e1360. 1157  
<https://doi.org/10.1002/wcms.1360> 1158  
Dovesi et al (2020) The CRYSTAL code, 1976–2020 and beyond, a long 1159  
story. *J Chem Phys* 152:204111. <https://doi.org/10.1063/5.0004892> 1160  
Eckardt RC, Byer RL (1991) Measurement of nonlinear optical 1161  
coefficients by phase-matched harmonic generation. In: Bor- 1162  
dui PF (ed) *Inorganic crystals for optics, electro-optics, and* 1163  
*frequency conversion*, SPIE, Proc. SPIE, vol 1561. <https://doi.org/10.1117/12.50759> 1164  
El-mallah H, Watts BE, Wanklyn B (1987) Birefringence of CaTiO<sub>3</sub> 1165  
and CdTiO<sub>3</sub> single crystals as function of temperature. *Phase* 1166  
*Transit* 9(3):235–245. <https://doi.org/10.1080/01411598708242352> 1167  
Evarestov RA (2007) *Quantum chemistry of solids. The LCAO first* 1168  
*principles treatment of crystals*. Springer, Berlin 1169  
Ferrari AM, Orlando R, Rérat M (2015) Ab initio calculation of the 1170  
ultraviolet-visible (UV-vis) absorption spectrum, electron-loss 1171  
function, and reflectivity of solids. *J Chem Theory Comput* 1172  
11(7):3245–3258. <https://doi.org/10.1021/acs.jctc.5b00199> 1173  
Ferrero M, Rérat M, Kirtman B, Dovesi R (2008a) Calculation of 1174  
first and second static hyperpolarizabilities of one- to three- 1175  
dimensional periodic compounds. Implementation in the 1176  
CRYSTAL code. *J Chem Phys* 129(24):244110. <https://doi.org/10.1063/1.3043366> 1177  
Ferrero M, Rérat M, Orlando R, Dovesi R (2008b) The calculation of 1178  
static polarizabilities of periodic compounds. The implementa- 1179  
tion in the CRYSTAL code for 1D, 2D and 3D systems. *J Comput* 1180  
*Chem* 29(9):1450–1459. <https://doi.org/10.1002/jcc.20905> 1181  
Fleischer M, Wilcox RE, Matzko JJ (1984) Microscopic determina- 1182  
tion of the nonopaque minerals. *U S Geol Surv Bull.* [https://doi.org/10.3133/b1627\\_1984](https://doi.org/10.3133/b1627_1984) 1183  
Garza AJ, Scuseria GE (2016) Predicting band gaps with hybrid den- 1184  
sity functionals. *J Phys Chem Lett* 7(20):4165–4170. <https://doi.org/10.1021/acs.jpcclett.6b01807> 1185  
Ghosh G (1999) Dispersion-equation coefficients for the refrac- 1186  
tive index and birefringence of calcite and quartz crystals. *Opt* 1187  
*Commun* 163(1–3):95–102. [https://doi.org/10.1016/S0030-4018\(99\)00091-7](https://doi.org/10.1016/S0030-4018(99)00091-7) 1188  
Halbout JM, Blit S, Donaldson W, Tang C (1979) Efficient phase- 1189  
matched second-harmonic generation and sum-frequency mixing 1190  
in urea. *IEEE J Quantum Electron* 15(10):1176–1180. <https://doi.org/10.1109/jqe.1979.1069900> 1191  
Hurst GJB, Dupuis M, Clementi E (1988) Ab initio analytic polariz- 1192  
ability, first and second hyperpolarizabilities of large conjugated 1193  
organic molecules: Applications to polyenes C<sub>4</sub>H<sub>6</sub> to C<sub>22</sub>H<sub>24</sub>. 1194  
*J Chem Phys* 89(1):385–395. <https://doi.org/10.1063/1.455480> 1195  
Kirtman B, Luis JM (2010) On the contribution of mixed terms in 1196  
response function treatment of vibrational nonlinear optical 1197  
properties. *Int J Quantum Chem* 111(4):839–847. <https://doi.org/10.1002/qua.22880> 1198  
Lacivita V, Rérat M, Kirtman B, Ferrero M, Orlando R, Dovesi R 1199  
(2009) Calculation of the dielectric constant  $\epsilon$  and first nonlinear 1200  
susceptibility  $\chi(2)$  of crystalline potassium dihydrogen phosphate 1201  
by the coupled perturbed Hartree-Fock and coupled perturbed 1202  
Kohn-Sham schemes as implemented in the CRYSTAL code. *J* 1203  
*Chem Phys* 131(20):204509. <https://doi.org/10.1063/1.3267048> 1204  
1205  
1206  
1207  
1208  
1209  
1210  
1211  
1212  
1213



- 1214 Lacivita V, Rérat M, Kirtman B, Orlando R, Ferrabone M, Dovesi R  
1215 (2012) Static and dynamic coupled perturbed Hartree–Fock vibra-  
1216 tional (hyper)polarizabilities of polyacetylene calculated by the  
1217 finite field nuclear relaxation method. *J Chem Phys* 137:014103.  
1218 <https://doi.org/10.1063/1.4731266>
- 1219 Lacivita V, D’Arco P, Orlando R, Dovesi R, Meyer A (2013) Anoma-  
1220 lous birefringence in andradite-grossular solid solutions: a quan-  
1221 tum-mechanical approach. *Phys Chem Miner* 40(10):781–788.  
1222 <https://doi.org/10.1007/s00269-013-0612-6>
- 1223 Lee C, Yang W, Parr RG (1988) Development of the Colle–Salvetti  
1224 correlation-energy formula into a functional of the electron den-  
1225 sity. *Phys Rev B* 37(2):785–789. <https://doi.org/10.1103/physrevb.37.785>
- 1226 Levine ZH, Allan DC (1993) Large local-field effects in the sec-  
1227 ond-harmonic susceptibility of crystalline urea. *Phys Rev B*  
1228 48(11):7783–7789. <https://doi.org/10.1103/physrevb.48.7783>
- 1229 Malitson IH (1962) Refraction and dispersion of synthetic sapphire. *J*  
1230 *Opt Soc Am* 52(12):1377. <https://doi.org/10.1364/JOSA.52.001377>
- 1231 Malitson IH (1963) A redetermination of some optical properties  
1232 of calcium fluoride. *Appl Opt* 2(11):1103–1107. <https://doi.org/10.1364/AO.2.001103>
- 1233 Marcaud G, Serna S, Karamanis P, Alonso-Ramos C, Roux XL, Ber-  
1234 ciano M, Maroutian T, Agnus G, Aubert P, Jollivet A, Ruiz-Carid-  
1235 dad A, Largeau L, Isac N, Cassan E, Matzen S, Dubreuil N, Rérat  
1236 M, Lecoœur P, Vivien L (2020) Third order nonlinear optical sus-  
1237 ceptibility of crystalline oxide yttria-stabilized zirconia. *Photon*  
1238 *Res* 8(2):110. <https://doi.org/10.1364/prj.8.000110>
- 1239 Maschio L, Rérat M, Kirtman B, Dovesi R (2015) Calculation of  
1240 the dynamic first electronic hyperpolarizability  $\beta(-\omega, \omega_1, \omega_2)$   
1241 of periodic systems. Theory, validation, and application to  
1242 multi-layer MoS<sub>2</sub>. *J Chem Phys* 143(24):244102. <https://doi.org/10.1063/1.4937770>
- 1243 McDowell K (1976) Exact static dipole polarizabilities for the excited  
1244 states of the hydrogen atom. *J Chem Phys* 65(7):2518–2521. <https://doi.org/10.1063/1.433455>
- 1245 Nye JF (1985) *Physical properties of crystals*. Oxford University Press,  
1246 Oxford
- 1247 Orlando R, Lacivita V, Bast R, Ruud K (2010) Calculation of the first  
1248 static hyperpolarizability tensor of three-dimensional periodic  
1249 compounds with a local basis set: A comparison of LDA, PBE,  
1250 PBE0, B3LYP, and HF results. *J Chem Phys* 132(24):244106.  
1251 <https://doi.org/10.1063/1.3447387>
- 1252 Orr B, Ward J (1971) Perturbation theory of the non-linear optical  
1253 polarization of an isolated system. *Mol Phys* 20(3):513–526. <https://doi.org/10.1080/00268977100100481>
- 1254 Otto P (1992) Calculation of the polarizability and hyperpolariz-  
1255 abilities of periodic quasi-one-dimensional systems. *Phys Rev B*  
1256 45(19):10876–10885. <https://doi.org/10.1103/physrevb.45.10876>
- 1257 Peintinger MF, Oliveira DV, Bredow T (2013) Consistent gaussian  
1258 basis sets of triple-zeta valence with polarization quality for solid-  
1259 state calculations. *J Comput Chem* 34(6):451–459. <https://doi.org/10.1002/jcc.23153>
- 1260 Perdew JP, Zunger A (1981) Self-interaction correction to density-  
1261 functional approximations for many-electron systems. *Phys Rev*  
1262 *B* 23(10):5048–5079. <https://doi.org/10.1103/physrevb.23.5048>
- 1263 Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approx-  
1264 imation made simple. *Phys Rev Lett* 77(18):3865–3868. <https://doi.org/10.1103/physrevlett.77.3865>
- 1265 Polyanskiy MN (2020) Refractive index database. <https://refractiveindex.info>
- 1266 Rérat M, Ferrero M, Amzallag E, Baraille I, Dovesi R (2008) Compari-  
1267 son of the polarizability of periodic systems computed by using  
1268 the length and velocity operators. *J Phys Conf Ser* 117:012023.  
1269 <https://doi.org/10.1088/1742-6596/117/1/012023>
- 1270 Rérat M, Maschio L, Kirtman B, Civalleri B, Dovesi R (2015) Com-  
1271 putation of second harmonic generation for crystalline urea  
1272 and KDP. An ab Initio approach through the coupled perturbed  
1273 Hartree–Fock/Kohn–Sham scheme. *J Chem Theory Comput*  
1274 12(1):107–113. <https://doi.org/10.1021/acs.jctc.5b00791>
- 1275 Rosker M, Cheng K, Tang C (1985) Practical urea optical parametric  
1276 oscillator for tunable generation throughout the visible and near-  
1277 infrared. *IEEE J Quantum Electron* 21(10):1600–1606. <https://doi.org/10.1109/jqe.1985.1072557>
- 1278 Saleh BEA, Teich MC (1991) *Fundamentals of photonics: electro-  
1279 optics*. Wiley, New York. <https://doi.org/10.1002/0471213748>
- 1280 Shannon RD, Shannon RC, Medenbach O, Fischer RX (2002) Refrac-  
1281 tive index and dispersion of fluorides and oxides. *J Phys Chem Ref*  
1282 *Data* 31(4):931–970. <https://doi.org/10.1063/1.1497384>
- 1283 Shelton DP (1986) Hyperpolarizability dispersion measured for Kr and  
1284 Xe. *J Chem Phys* 84(1):404–407. <https://doi.org/10.1063/1.450152>
- 1285 Singh S (1986) CRC handbook of laser science and technology, sup-  
1286 plement 2: optical materials. In: Weber MJ (ed) *Laser & optical*  
1287 *science & technology*. CRC Press, Boca Raton, pp 147–250
- 1288 Stephens RE, Malitson IH (1952) Index of refraction of magne-  
1289 sium oxide. *J Res Natl Bur Stand* 49(4):249–252. <https://doi.org/10.6028/jres.049.025>
- 1290 Torrent-Sucarrat M, Solà M, Duran M, Luis JM, Kirtman B (2004)  
1291 Basis set and electron correlation effects on initial conver-  
1292 gence for vibrational nonlinear optical properties of conjugated  
1293 organic molecules. *J Chem Phys* 120(14):6346–6355. <https://doi.org/10.1063/1.1667465>
- 1294 Traini M (1996) Electric polarizability of the hydrogen atom:  
1295 a sum rule approach. *Eur J Phys* 17(1):30–36. <https://doi.org/10.1088/0143-0807/17/1/006>
- 1296 Wright FE (1951) Computational of the optic axial angle from the  
1297 three principal refractive indices. *Am Mineral* 36(7–8):543–556
- 1298 Yakovkin IN, Dowben P (2007) The problem of the band gap in LDA  
1299 calculations. *Surf Rev Lett* 14:481–487. <https://doi.org/10.1142/S0218625X07000949>

**Publisher’s Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.