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Dovesi

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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

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

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

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#### From anisotropy of dielectric tensors to birefringence: a quantum 2 mechanics approach 3

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> 4

5 Received: 11 February 2020 / Accepted: 3 July 2020

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#### 7 Abstract

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8 The way quantum mechanical ab initio computer codes allow to compute, through perturbation theory (the so-called SC-CP, 9 self-consistent coupled-perturbed scheme), many properties resulting from the interaction of the electric field with a crystal-10 line system is illustrated. The polarizability, which leads to the dielectric tensors as well as to the refractive indices and to 11 he birefringence of materials, is the simplest on this list. Higher order tensors, like the first and second hyperpolarizabilities, 12 can be obtained as well with the CRYSTAL code here used. These properties, resulting from the Taylor expansion of the 13 total energy of the solid as a function of the electric field, belong to a large family of phenomena generated by combining in 14 different ways the frequencies of the fields. Second-harmonic generation (SHG), Pockels effect, intensity-dependent refrac-15 tive index (IDRI), and other quantities now accessible to experiment can be computed at a relatively low cost and with high 16 accuracy.

17 **Keywords** Refractive index · Birefringence · (Non)linear electric susceptibility tensor · Anisotropy · Quantum mechanical 18 simulation · CRYSTAL code · Gaussian-type basis set

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- 20

This paper is the peer-reviewed version of a contribution presented A1 at the Conference on Anisotropic Properties of Matter, organized Δ2

by Giovanni Ferraris and held at Accademia Nazionale dei Lincei A3 in Rome, October 16-17, 2019.

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Michel Rérat A5 michel.rerat@univ-pau.fr A6

1 Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, Α7 IPREM, 2 av. président P. Angot, 64053 Pau, France A8

- 2 Sorbonne Université, CNRS-INSU, ISTeP UMR 7193, A9 75005 Paris, France A10
- Advanced Materials Lab, Samsung Research America, 10 A11 Wilson Rd., Cambridges, MA 02138, USA A12
- 4 Sorbonne Université, CNRS, IMJ UMR 7586, 75005 Paris, A13 France A14
- A15 Université de Lorraine-Nancy, CNRS, Laboratoire de Physique et Chimie Théoriques, UMR 7019, A16 Vandoeuvre-les-Nancy, France A17
- Dipartimento di Chimica, Nanostructured Interfaces A18 A19 and Surfaces (NIS) Centre of Excellence, Università di Torino, Via P. Giuria 7, 10125 Turin, Italy A20

# 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

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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:

where  $\boldsymbol{\mu}_0, \boldsymbol{\alpha}_0, \boldsymbol{\beta}_0$ , and  $\boldsymbol{\gamma}_0$  are the permanent dipole moment, 99 polarizability, and first and second hyperpolarizabilities 100 of the free system, respectively (the conventional nega-101 tive sign is such that the dipole moment is defined as the 102 sum over the charges multiplied by their position, and such 103 that the polarizability of the ground state is positive). The 104 symbol  $\otimes$  indicates the outer product of vectors. Given 105 the electric field conversion coefficient from the atomic 106 units (a.u.) system to the international system of units 107 (SI): 1 a.u. =  $5.14 \times 10^{11}$  Vm<sup>-1</sup>, a large static field of say 108  $50 \,\mathrm{kV cm^{-1}}$  (maximum field amplitude that can be applied 109 with electrodes at the surface of a slab before electric break-110 down), is smaller than  $10^{-5}$  a.u.. If we apply a field of this 111 amplitude to a molecule, say water, with a polarizability 112 equal to  $\sim 10 \text{ bohr}^3$  (the polarizability unit is equivalent to 113 a volume in a.u.), the energy variation due to the polariza-114 tion would be equal to  $10^{-9} E_h$ . As the ratio between the 115 terms appearing in Eq. 2  $(\beta_0 / \alpha_0, \gamma_0 / \beta_0)$  is generally smaller 116 than  $10^3$  a.u., to be multiplied by an additional field intensity 117 of  $10^{-5}$ , it is clear that contributions approach rapidly the 118 numerical accuracy limit of quantum mechanical calcula-119 tions. This is why,  $\beta_0$  and  $\gamma_0$  coefficients have been con-120 sidered in the past of low interest, and terms as  $\delta_0$ , corre-121 sponding to power five of  $\mathbf{E}_0$ , have been neglected in Eq. 2. 122 However, if the expanded quantity is not the total energy, 123 but some higher term evaluated analytically, then the power 124 of  $\mathbf{E}_0$  for obtaining  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  is lower. This is the case, for 125 example, when the polarizability  $\boldsymbol{\alpha}_0$  is computed analyti-126 cally, with a reduction by 2 of the power of  $E_0$ . Moreover, 127 lasers with much higher intensity than static electric fields 128 are now available, which can allow to access experimen-129 tally many non-negligible second- and third-order non-linear 130 optical (NLO) effects. 131

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

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

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

The larger the matrices, the more accurate the calculation.
Obviously, this kind of linear algebra requires the use of

47 computers (clusters of PC) or supercomputers containing
 48 10<sup>2</sup>-10<sup>4</sup> processors.

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

where  $\hat{H}$  is an operator, called Hamiltonian in memory of classical mechanics developed by Lagrange (1736–1813) and then Hamilton (1805–1865), and  $\mathscr{E}$  the energy associated to the wavefunction  $\Psi$ .

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 Schröding-62 er's 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 reasonable accuracy the ground state of a crystalline system.

78 We are then faced with the problem of the description 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 electric field operating on it. What is the information that can be obtained as a response of the system to this perturbation? Let

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- Obviously, the various electric fields can depend on 142 (c) frequency as in light radiation,  $\mathbf{E} \equiv \mathbf{E}(\omega) = \mathbf{E}_0 \cos(\omega t)$ 143 with the angular  $\omega$ -frequency of the corresponding pho-144 ton ( $\hbar\omega$  with  $\hbar = h/2\pi$ , h being the Planck constant 145 equal to  $6.63 \times 10^{-34}$  Js), further increasing the number 146 of possible ways of perturbing the system. For example, 147 in the second-harmonic generation (SHG) experiments, 148 interaction of light with matter can provide one scat-149 tered photon of energy  $\hbar 2\omega$  from two photons of energy 150  $\hbar\omega$ , the intensity of the scattering light depending on 151 the frequency-dependent first hyperpolarizability, 152  $\beta(-2\omega;\omega,\omega)$ , of the material, as we will see later on. 153
- As a corollary to point (c), the frequency can be used (d) 154 for perturbing both nuclei and electrons, or just the lat-155 ter. 156

The following section will deepen some of the main topics 157 introduced here. 158

#### 2 Methods 159

#### 2.1 Dipole moment and (hyper)polarizability 160

#### 2.1.1 Definitions 161

The dipole moment  $\mu$  of a finite system is a vector defined, 162 in the atomic unit system, as: 163

$$\mu = \sum_{N} Z_{N} \mathbf{r}_{N} - \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}, \qquad (3)$$

where the absolute value of the electron charge is equal to 1 166 (e = -1 a.u.).  $Z_N$  and  $\mathbf{r_N}$  are the nuclear charge and position 167 of the *N*th atom, and  $\rho(\mathbf{r})$  is the electron charge density in  $\mathbf{r}$ . 168 For a given geometry,  $Z_N$  and  $\mathbf{r}_N$  are fixed, and the value of 169 the dipole moment can be obtained if the electron density is 170 known in the whole space. In quantum chemistry, this latter, 171 which is the square of a wave function,  $\Psi$ , describing the 172 electronic state of the system (generally its ground state) can 173 be obtained by solving the time-independent Schrödinger's 174 equation (see Eq. 1). Using Dirac's notation,  $\int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}$  in 175 Eq. 3 can now be replaced by  $\langle 0|\mathbf{r}|0\rangle$  where  $\langle 0|$  and  $|0\rangle$  rep-176 resent the bra and ket of the ground state. 177

In the presence of a time-dependent electromagnetic 178  $(\mathbf{E}(\mathbf{r},t), \mathbf{B}(\mathbf{r},t))$  field, the expression of  $\hat{H}$  becomes: 179

<sup>180</sup> 
$$\hat{\mathbf{H}} = \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t) \right)^2 + eU(\mathbf{r}, t) + V_C(\mathbf{r}), \tag{4}$$

where **p** and **r** are the momentum and position of the electron, 182 *m* its mass (m = 1 a.u.), *c* the speed of light (c = 137. a.u.), 183 and  $V_C$  the Coulomb potential. The electromagnetic field is 184

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

$$\mathbf{E}(\mathbf{r},t) = -\frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} - \nabla U(\mathbf{r},t)$$
(5)
<sup>187</sup>
<sub>188</sub>

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

and there is an infinite number of  $(\mathbf{A}(\mathbf{r},t),\mathbf{U}(\mathbf{r},t))$  couples 191 describing one electromagnetic field. Obviously, the solu-192 tions of the time-dependent Schrödinger's equation must be 193 independent from the choice of the so-called gauge. This 194 is indeed the case of the energy *E*-eigenvalue as well as of 195  $|\Psi(\mathbf{r},t)|^2$ . Only the phase of the wave function depends on 196 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 198 number:  $q = 2\pi/\lambda$  compared to **r** (i.e., for  $\lambda$ -wavelength 199 much larger than the size of the studied system:  $\lambda \gg 1$  Å), 200  $\mathbf{E}(\mathbf{r})$  is generally defined from the scalar potential only as 201 follows: 202

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

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

$$\hat{\mathbf{H}} = \frac{\mathbf{p}^2}{2m} + V_C(\mathbf{r}) - e\mathbf{r} \cdot \mathbf{E}_0 = \hat{\mathbf{H}}_0 - e\mathbf{r} \cdot \mathbf{E}_0$$
(8)
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in the electric dipole moment approximation for finite systems (0D or molecules),  $\hat{H}_0$  being the Hamiltonian operator of the unperturbed system.

The energy  $\mathscr{E}$  of the molecule in presence of the  $\mathbf{E}_0$ -field 211 can be developed as a Taylor series as shown in Eq. 2; simi-212 larly, for the dipole moment, we have: 213

$$\boldsymbol{\mu} = -\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\mathbf{E}_{0}} = \boldsymbol{\mu}_{0} + \boldsymbol{\alpha}_{0}\mathbf{E}_{0} + \frac{1}{2!}\boldsymbol{\beta}_{0}\mathbf{E}_{0}\otimes\mathbf{E}_{0}$$

$$+\frac{1}{3!}\boldsymbol{\gamma}_{0}\mathbf{E}_{0}\otimes\mathbf{E}_{0}\otimes\mathbf{E}_{0} + \cdots,$$
(9)

where  $\mu_0$  is the permanent dipole moment of the molecule, 216 the linear response  $\alpha_0$  is called the polarizability, and  $\beta_0$ 217 and  $\gamma_0$  are the first and second hyperpolarizabilities. The 218 previous electric responses to the electric field are intrinsic 219 properties of the molecule: they are equal to the first, second, 220 and third derivatives of the induced dipole moment  $(\boldsymbol{\mu} - \boldsymbol{\mu}_0)$ 221 with respect to the field  $\mathbf{E}_0$ , at zero field  $(\mathbf{E}_0 \rightarrow \mathbf{0})$ . Moreo-222 ver, being  $\mu_0$  and  $\mathbf{E}_0$  vectors,  $\boldsymbol{\alpha}_0$ ,  $\boldsymbol{\beta}_0$  and  $\boldsymbol{\gamma}_0$  are tensors of rank 223 2, 3, and 4, respectively. 224

In the case of a frequency-dependent electric field 225  $(\mathbf{E}(\omega) = \mathbf{E}_0 \cos \omega t)$ , the linear term of the dipole moment 226 induced by the oscillating field is oscillating at the same fre-227 quency of the field (forced oscillation if the field frequency 228 is small compared to proper resonance frequencies of the 229 system) leading to a frequency-dependent polarizability, 230  $\alpha(\omega)$ . For a molecule in its electronic ground state (|0)), 231

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

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

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

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

The associated mean value oscillator strengths:

$$f_n = \frac{2}{3}\omega_n \langle 0|\mathbf{r}|n\rangle^2 \tag{11}$$

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

See the work of Orr and Ward (1971) for the expression of hyperpolarizabilities.

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

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

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where  $\omega_i$  is the frequency of the normal mode  $(Q_i)$  and  $\sigma_i$  the Born charge  $(d\mu_0/dQ_i \text{ with } \mu_0 \text{ as defined in Eq. } 3$  at zero field) obtained at the equilibrium geometry. The  $(\omega_i, \sigma_i)$  couples reproduce the infrared (IR) spectrum.

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

 $\alpha^{nr}$  is zero in purely covalent materials as diamond or sili-263 con, and also negligible for other ionic materials if the field 264 frequency  $(\omega)$  corresponds to the UV-visible range of 265 energy  $\omega \gg \omega_i$ . Indeed, the Born charge  $d\mu_0/dQ_i$ , which is 266 actually a charge divided by the square root of ion mass, is 267 small with respect to 1 a.u., and  $\sigma_i^2/(\omega_i^2 - \omega^2) \simeq -\sigma_i^2/\omega^2$ , 268 which is then negative, becomes very small in absolute val-269 ues compared to the static vibrational polarizability contri-270 bution:  $\sigma_i^2 / \omega_i^2$ . 271

Also the vibrational contribution to  $\beta$  and  $\gamma$  can be neglected in the UV-visible frequency range for the same reason as for  $\alpha$ , if all the external fields are frequencydependent. The exception is the particular case of the intensity-dependent refractive index, IDRI, a process depending on  $\gamma(-\omega; \omega, -\omega, \omega)$ , that includes terms with opposite sign

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phases,  $\pm \omega$ , generating then a static field and a vibrational contribution. 278

#### 2.1.2 Calculation of the microscopic response properties 280

The electronic contribution to the polarizability (Eq. 10) is a 281 second-order perturbation energy, the expression of which is 282 a sum extended to an infinite number of excited state terms, 283 a series which generally converges very slowly. Moreover, 284 it also depends on the continuum. For example, if we use 285 all the true (and well known) discrete spectral states of the 286 H atom, its polarizability value is less than 4 bohr<sup>3</sup>, while 287 its exact value is 9/2 bohr<sup>3</sup> (without taking into account the 288 relativistic effect) (Coulson 1941; McDowell 1976; Traini 289 1996; Bishop 1999). 290

Fortunately, it is not necessary to know all the excited 291 discrete and continuum states of the electronic system to 292 obtain a "good" static polarizability value, or dynamic polar-293 izabilities for a field frequency smaller than the first reso-294 nance one. The coupled-perturbed Hartree-Fock (CPHF) 295 method proposed by Hurst et al. (1988), consisting in the 296 independent-particle model using relaxed occupied and vir-297 tual orbitals via a self-consistent process in the presence of 298 the external field, generally leads to results in good agree-299 ment with the experiments, in particular when a density 300 functional theory (DFT) Hamiltonian with a percentage of 301 the exact or Hartree-Fock (HF) non-local exchange potential 302 is used, as is the case of the hybrid B3LYP (Becke 1993; 303 Lee et al. 1988) functional (20% of HF exchange). Indeed. 304 response properties which are n-order perturbation energies 305 depend strongly on the band gap (which determines the low-306 est transition energy values,  $\omega_n \geq \text{gap}$ , on the denominator 307 of Eq. 10 for electronic polarizability, and of hyperpolariz-308 abilities), generally too large with HF (Evarestov 2007) and 309 too small with pure DFT (Yakovkin and Dowben 2007), but 310 reasonably described by hybrids (Garza and Scuseria 2016). 311

#### 2.1.3 Infinite periodic systems

Expression 8 of the Hamiltonian, that includes the position 313 operator, **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 presence of a constant field, or a field with a large  $\lambda$  wavelength 317 with respect to the size of the electronic system ( $\lambda \gg 1$ Å). 318

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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. 326

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

$$\hat{\Omega}_{k} = \mathbf{r} + \imath \nabla_{k} = -\imath e^{-\imath \mathbf{k} \cdot \mathbf{r}} \nabla_{k} e^{\imath \mathbf{k} \cdot \mathbf{r}}, \qquad (13)$$

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

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

### 354 2.2 Refractive index

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

#### 360 2.2.1 Definition

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

<sup>364</sup> 
$$\mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E} - \frac{\xi}{c} \frac{\partial \mathbf{H}}{\partial t}$$
 (14)

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$$\mathbf{B} = \boldsymbol{\mu}_r \boldsymbol{\mu}_0 \mathbf{H} + \frac{\boldsymbol{\xi}}{c} \frac{\partial \mathbf{E}}{\partial t},\tag{15}$$

where  $\epsilon_r$  and  $\mu_r$  are the relative electric permittivity and magnetic permeability (matrices) of the medium, respectively;  $\epsilon_0$  and  $\mu_0$  are the permittivity and permeability (constants) of the vacuum, such that  $\mu_0 \epsilon_0 c^2 = 1$ ; and  $\xi$  is the chirality (matrix) responsible of the rotation angle of a polarized electromagnetic field.

Then, for materials with  $\mu_r \simeq 1$  (low magnetic permeability) and  $\xi = 0$  (no chirality), the refractive index is (Condon 1937): 376

$$\mathbf{n} = \left( (\boldsymbol{\mu}_r \boldsymbol{\epsilon}_r)^{-\frac{1}{2}} \pm \omega \boldsymbol{\xi} \right)^{-1} \simeq \sqrt{\boldsymbol{\epsilon}_r}.$$
(16)
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#### 2.2.2 Optical indicatrix and birefringence

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

$$\frac{X^2}{n_X^2} + \frac{Y^2}{n_Y^2} + \frac{Z^2}{n_Z^2} = 1$$
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and with semi-axis lengths given by the square roots of the dielectric tensor eigenvalues,  $n_i = \sqrt{\epsilon_i}$  (i = X, Y, Z), corresponding to the *principal refractive indices* of the medium. We will assume that the indices along the semi-axis *X*, *Y*, *Z*, are ordered by increasing value. 386 387 388 389 389 389 390

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  $n_{\varepsilon}$ . 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  $\delta = |n_e - n_{\omega}|$ . 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  $(n_{\epsilon} = n_{\chi}, n_{\omega} = n_{\chi} = n_{\chi})$ , 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

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**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  $n_{\omega}$ , and  $n_Z$  is indicated as  $n_e$ ; the two circular sections merge in a single one orthogonal to *Z* 

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

#### 421 2.2.3 Non-linear optics and birefringence

Intense electric fields can also provide birefringence as dem-onstrated in the following.

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

<sup>425</sup> 
$$\mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E} = \epsilon_0 \mathbf{E} + \mathbf{P},$$
 (17)

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

<sup>430</sup> 
$$\mathbf{P} = \epsilon_0 (\boldsymbol{\chi}^{(1)} \mathbf{E} + \boldsymbol{\chi}^{(2)} \mathbf{E} \otimes \mathbf{E} + \boldsymbol{\chi}^{(3)} \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} + \cdots),$$
 (18)  
<sup>431</sup>

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 **E** produced by the light wave of frequency  $\omega$  together with an external static electric field **E**<sub>0</sub>:

where  $\mathbf{E}_{\omega}$  is the vector amplitude of the wave. Then, a nonzero component value of  $\chi^{(2)}$  leads to an additive term proportional to  $\mathbf{E}_0$ -modulus in the expression of the polarization vector which oscillates with the same  $\omega$  frequency as the electromagnetic field: 442

$$\mathbf{P}(\omega) = \boldsymbol{\varepsilon}_0(\boldsymbol{\chi}_{(-\omega;\omega)}^{(1)} + 2\boldsymbol{\chi}_{(-\omega;\omega,0)}^{(2)}\mathbf{E}_0)\mathbf{E}_\omega\cos\omega t, \qquad (20) \qquad 444$$

and induces a linear variation of the refractive index with  $^{446}$  respect to the modulus of  $E_0$ :  $^{447}$ 

$$\mathbf{n}(\omega) = \sqrt{\mathbf{1} + \boldsymbol{\chi}_{(-\omega;\omega)}^{(1)} + 2\boldsymbol{\chi}_{(-\omega;\omega,0)}^{(2)} \mathbf{E}_0}$$

$$\simeq \mathbf{n}_0(\omega) + \mathbf{n}_0(\omega) \mathbf{E}_0$$
(21)

with

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

$$451$$

$$452$$

This Pockels effect responsible of the birefringence: 453  $\Delta \mathbf{n} = \mathbf{n}_1 \mathbf{E}_0$ , depends on the odd rank tensor,  $\chi^{(2)}$ , which is 454 null for materials with an inversion symmetry. However, the 455 birefringence of centrosymmetric materials can be seen if 456 they own a large third-order non-linear  $\chi^{(3)}$  susceptibility 457 (tensor of rank four) and for intense electric fields. Indeed, 458 it comes from the quadratic term in E in the polarization 459 vector expression (Eq. 18). In the intensity-dependent refrac-460 tive index (IDRI) Kerr effect (see Boyd 2003), an intense 461 beam of light in the crystal can itself provide the modulating 462 electric field: 463

$$\mathbf{E} = \mathbf{E}_{\omega} \cos \omega t = \frac{1}{2} \mathbf{E}_{\omega} \left( e^{i\omega t} + e^{-i\omega t} \right)$$
(22) 464

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: 469

$$\mathbf{P}(\omega) = \boldsymbol{\epsilon}_0 \Big( \boldsymbol{\chi}_{(-\omega;\omega)}^{(1)} + \frac{3}{4} \boldsymbol{\chi}_{(-\omega;\omega,-\omega,\omega)}^{(3)} \mathbf{E}_{\omega}^2 \Big) \mathbf{E}_{\omega} \cos \omega t, \qquad (23)$$
<sup>470</sup>

and then, we have:

$$\mathbf{n}(\omega) \simeq \mathbf{n}_0(\omega) + \frac{3}{8n_0(\omega)} \boldsymbol{\chi}^{(3)}_{(-\omega;\omega,-\omega,\omega)} \mathbf{E}^2_{\omega}$$
<sup>473</sup>
<sup>(24)</sup>

$$\simeq \mathbf{n}_0(\omega) + \mathbf{n}_2(\omega)\mathbf{I}$$

with **I** the light intensity. In that case, the birefringence is given by  $\mathbf{n}_2$ , i.e., by the IDRI-Kerr non-linear electric  $\chi^{(3)}_{(-\omega;\omega,-\omega,\omega)}$  susceptibility. 477

A recent application referring to yttria-stabilized zirconia 478 can be found in Marcaud et al. (2020). Several other NLO 479 processes also appear when combining the Taylor develop-480 ment of the polarization vector shown in Eq. 18 with the 481 field expression given in Eq. 19 (see Saleh and Teich 1991; 482 Boulon 2001), as SHG linked to  $\chi^{(2)}(-2\omega;\omega,\omega)$  and third 483 harmonic generation (THG) linked to  $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ , but 484 they do not affect the refractive index at  $\omega$ -frequency. 485

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#### 2.2.4 Relation between (non)linear susceptibilities 486 and (hyper)polarizabilities 487

The macroscopic (non)linear optical properties,  $\chi^{(n)}$ , in the 488 expression (Eq. 18) of the polarization vector are linked to 489 the microscopic  $\alpha, \beta, \gamma \cdots$  (hyper)polarizability properties 490 of a unit cell of the material, recalling that **P** is the dipole 491 moment per unit cell volume V induced by the mean (mac-492 roscopic) field (E) felt by the cell, and that can be also 493 developed as follows: 494

<sup>495</sup> 
$$\mathbf{P} = \frac{1}{V} \Big( \boldsymbol{\alpha} \mathbf{E} + \frac{1}{2!} \boldsymbol{\beta} \mathbf{E} \otimes \mathbf{E} + \frac{1}{3!} \boldsymbol{\gamma} \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} + \cdots \Big).$$
(25)  
<sup>496</sup>

The relative electric permittivity (or dielectric matrix)  $\epsilon_r$  at 497 zero field is then linked to the polarizability  $\alpha$  of the unit 498 cell: 499

$$\varepsilon_r = \mathbf{1} + \boldsymbol{\chi}^{(1)} = \mathbf{1} + \frac{1}{\varepsilon_0} \boldsymbol{\alpha} / V, \qquad (26)$$

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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 502 503 atomic units. 504

It follows that the  $\alpha$ ,  $\beta$ , and  $\gamma$  tensors obtained from the 505 SC-CP calculation discussed in Sect. 2.1.3 for infinite peri-506 odic systems allow to determine the (non)linear suscep-507 tibilities,  $\chi^{(n)}$ , and the refractive index and birefringence. 508

#### **3** Applications and comparison 509 with experimental data 510

The examples should provide an idea of the quality of the 511 results that can be obtained by simulation, and in particu-512 lar with the CRYSTAL code (Dovesi et al. 2017, 2018, 513 2020). 514

Before illustrating these examples, it should be mentioned 515 that (obviously) the results depend deeply on the computa-516 tional parameters; the most important are listed below: 517

The variational basis set: in the following examples, a 518 localized Gaussian basis set in split valence or multi-519 ple zeta forms, usually including polarization functions, 520 is used. This is in general sufficient to provide accurate 521 results. 522

The level of the theory: all calculations are performed 523 at the DFT level, and the most reliable, in our opinion, 524 are obtained with hybrid functionals, containing a frac-525 tion of the exact Hartree-Fock exchange. However, as the 526 superiority of one functional with respect to the others is 527 frequently a matter of discussion, in some cases we will 528 compute the same property with various functionals. 529

The intrinsic numerical accuracy of the implemented 530 algorithms, that in the CRYSTAL code is very high, so 531 that its influence on the final results can be considered 532 negligible. 533

One additional point must be underlined, when comparing 534 simulation and experiments: the experimental determina-535 tions to be compared with are, in many cases, scarce, or 536 affected by large uncertainty, so that error bars on the two 537 sides (simulation and experiment) should be considered. 538 Just to mention an example: the complete determination 539 of all components of a tensor (and many of the ones men-540 tioned above are third or fourth-order tensors, with many 541 components) requires that the experiment is repeated 542 with different orientations of the crystal, possibly with 543 various polarization of the light. The obtained results are 544 often not directly the specific constant to be inserted in 545 the tensor table, but a linear combination of them gener-546 ating a system of (linear) equations, whose solution (in 547 particular when small and large numbers are involved) can 548 produce strongly correlated final values. The uncertainty 549 is increased in some cases by the fact that, intrinsically, 550 the experiment is unable to determine the signs of the 551 constants. 552

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 560 properties listed above, when referred to a gas or a liquid, 561 reduces to the trace (for order two tensors) or to a few 562 invariants (for higher order tensors). In the solid state, on 563 the contrary, all specificity related to orientation is con-564 tained in the tensor. Tensors are defined with reference to 565 a cartesian frame (there are rules for defining the orien-566 tation of the lattice vectors with respect to the cartesian 567 frame), so that the constants take the following form, for a 568 fourth-order tensor:  $T_{ijkl}$ , where i, j, k, l can be x, or y or z. 569 The first manifestation of anisotropy is that some of these 570 components are null for symmetry reasons. Or, viceversa, 571 if the components that should be null are not, some sort 572 of deformation of the lattice with respect to the ideal situ-573 ation must be taken into account. 574

The examples refer to the (hyper)polarizabilities of pol-575 yacetylene (PA) for which both electronic and ionic contri-576 butions are important, the NLO properties of benchmarks 577 as urea ( $CH_4N_2O$ ) and potassium di-hydrogen phosphate 578 (KDP, KH<sub>2</sub>PO<sub>4</sub>), and the birefringence of a series of uni-579 axal and biaxal minerals. 580

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

The electronic (hyper)polarizabilities (with zero-point 583 averaging included) which are calculated from the SC-CP 584 method described above do not take into account the so-585 called *pure* vibrational effects, which can be quite important. 586 In the CRYSTAL code, these ionic effects are taken into 587 account analytically for the polarizability,  $\alpha$  (Eq. 12), and for 588 the first hyperpolarizability,  $\beta$  (Eq. 6 of Rérat et al. 2015), 589 from the IR and Raman spectra, but not for  $\gamma$ , the second 590 hyperpolarizability (hyper-Raman data are also required; see 591 Champagne et al. 1997). 592

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 596 CRYSTAL code before SC-CP, to compute numerically the 597 598 static response properties of molecules and periodic systems (see Darrigan et al. 2003). Using then, the finite field 599 nuclear relaxation (FF-NR) scheme of Bishop et al. (1995) 600 that mixes the FF and SC-CP methods, several NLO pro-601 cesses due to the second hyperpolarizabilities can be studied 602 by fitting the Taylor developments of the dipole moment, 603 polarizability, and first hyperpolarizability with respect to 604 the static finite field E, at the equilibrium geometry opti-605 mized in the presence of the field or not,  $\mathbf{R}_{E}$  and  $\mathbf{R}_{0}$  respec-606 tively. For example, the Taylor development of the SC-CP 607 (electronic) polarizability is: 608

<sup>609</sup> 
$$\alpha_{tu}^{e}(\mathbf{R}_{0}, \mathbf{E}) = \alpha_{tu}^{e}(\mathbf{R}_{0}, \mathbf{0}) + \sum_{v} \beta_{tuv}^{e} \mathbf{E}_{v}$$
  
+  $\frac{1}{2} \sum_{v,w} \gamma_{tuvw}^{e} \mathbf{E}_{v} \mathbf{E}_{w} + \cdots$  (27)

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<sup>611</sup> 
$$\alpha_{tu}^{e}(\mathbf{R}_{E}, \mathbf{E}) = \alpha_{tu}^{e}(\mathbf{R}_{0}, \mathbf{0}) + \sum_{v} b_{tuv}^{\alpha} \mathbf{E}_{v} + \frac{1}{2} \sum_{v,w} g_{tuvw}^{\alpha} \mathbf{E}_{v} \mathbf{E}_{w} + \cdots, \qquad (28)$$

612 613

where:

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

$$\begin{cases} 616 \\ g_{tuvw}^{\alpha} = \gamma_{tuvw}^{e} + \gamma_{tuvw}^{nr} (-\omega; \omega, 0, 0)|_{\omega \to \infty}. \end{cases}$$
(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 the624static field should lead, in principle, to linear terms identical625to the electronic and total static polarizabilities, the latter626being the sum of the electronic (Eq. 10) and nuclear relaxa-627tion (Eq. 12) contributions to the polarizability:628

$$\boldsymbol{\alpha}^{\mu} = \boldsymbol{\alpha}^{e+nr} = \boldsymbol{\alpha}^{e} + \boldsymbol{\alpha}^{nr}, \tag{31}$$

since, in either case, only harmonic vibrational terms are 631 included. However, the static hyperpolarizabilities also con-632 tain contributions due to anharmonic force constants and 633 anharmonic electrical property derivatives (see, for example, 634 Torrent-Sucarrat et al. 2004). To isolate the nuclear relaxa-635 tion term, one can either subtract the analytically determined 636 electronic term or calculate the difference between numeri-637 cal values from the Taylor developments with and without 638 geometry optimization in the presence of the static field. 639 When the geometry is not specified, it is  $\mathbf{R}_0$ ; the omitted 640 frequencies are zero. The subscript  $\omega \to \infty$  in Eqs. 29 and 641 30 refers to the infinite optical frequency (high-frequency or 642 UV-visible frequency) approximation. In addition to har-643 monic terms, first-order anharmonic contributions are also 644 included for  $\gamma^{nr}(-\omega;\omega,0,0)|_{\omega\to\infty}$  with this FF-NR method 645 (see Bishop et al. 1995); for the other two NLO processes, 646  $\beta^{nr}(-\omega;\omega,0)|_{\omega\to\infty}$  and  $\gamma^{nr}(-2\omega;\omega,\omega,0)|_{\omega\to\infty}$  (the latter being 647 obtained from fits of  $\beta^{e}$ ), the first-order anharmonicity terms 648 vanish. 649

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).

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Let us consider now the case of all-trans polyacetylene 657 (PA) (Lacivita et al. 2012), lying in the xy plane, with alter-658 nating double and single C-C bonds along the x periodic 659 direction (a double C-C bond is included within each unit 660 cell). The center of the unit cell is an inversion point (which 661 annihilates odd order energy perturbation terms, i.e.,  $\mu$  and 662  $\beta$  in our case) and lies on a  $C_2$ -axis perpendicular to the  $\sigma_h^{XY}$ 663 mirror plane, which relates z and -z directions, so that all the 664 components of the  $\alpha$  and  $\gamma$  tensors containing an odd number 665 of z indices vanish. 666

A finite field is applied along the non-periodic directions 667 (y, z, and mixed yz) to obtain the various non-zero inde-668 pendent tensor components of the vibrational (hyper)polariz-669 abilities.  $\gamma$  is a fourth-order tensor consisting, in principle, of 670  $3^4 = 81$  components,  $\gamma_{tuvw}$ . Several components are, however, 671 null or equivalent either by point symmetry or permutation 672 of indices, the latter depending on the number of static field 673 indices. For example, in the case of  $\gamma_{tuVW}^{nr}(-\omega;\omega,0,0)|_{\omega\to\infty}$ , 674 only the permutations  $\mathscr{P}_{t,u}$  (associated with the  $\omega \to \infty$ 675

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

680 (a) 
$$\gamma_{4,tuvw}^{nr} = \gamma_{TUVW}^{nr}(0;0,0,0),$$

and

681 (b) 
$$\gamma_{2,tuvw}^{nr} = \gamma_{tuVW}^{nr} (-\omega;\omega,0,0)|_{\omega \to \infty}$$

682

683 (c) 
$$\gamma_{1,tuvw}^{nr} = \gamma_{tuvW}^{nr} (-2\omega; \omega, \omega, 0)|_{\omega \to \infty}$$
.

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

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

In the longitudinal x-direction of PA, no components of 706  $\gamma$  can be calculated from the fit of the dipole moment with 707 respect to static fields, since its  $\mu_x$ -component is ill-defined. 708 Then, only components of  $\gamma$  having 1, 2, or 3 x-indices can 709 be obtained from fits of  $\alpha_{xy(z)}^e$  and  $\beta_{xyz}^e$ ,  $\alpha_{xx}^e$  and  $\beta_{xxy(z)}^e$ , and  $\beta_{xxx}^e$ 710 with respect to static  $E_v$  and  $E_z$  fields. This means that at least 711 one field must be frequency-dependent, leading then to a 712 small nuclear relaxation contribution  $\gamma_1^{nr}$  to  $g^{\beta}$  with respect 713 to the electronic one. However, the vibrational contribution 714 is larger than the electronic one for the two-static field  $g^{\alpha}$ 715 non-linear optic property, particularly when both in-plane 716 periodic x and non-periodic y components are involved. In 717 the case of  $\gamma_{xxyy}(-\omega;\omega,0,0)$ , the vibrational contribution,  $\gamma_2^{nr}$ , 718 is equal to  $+2.332 \times 10^4$  a.u., while the total value is smaller: 719  $g^{\alpha} = +9877$  a.u., showing that the electronic contribution 720 has an opposite sign with respect to the vibrational contribu-721 tion, being equal to  $-1.334 \times 10^4$  a.u. 722

It is worth noting that  $\gamma_{xxxx}^{nr}$  for the intensity-dependent 723 refractive index (IDRI) process depends on the Raman inten-724 sities only, as  $\alpha_{xx}^{nr}$  depends on the IR intensities, and can be 725 directly obtained as follows (Champagne et al. 1997): 726

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

The CRYSTAL code computes the Raman intensities, and 729 then allows to analytically obtain this parallel IDRI vibra-730 tional contribution too, which is of the same order of mag-731 nitude as the electronic one, around  $6 \times 10^{6}$  a.u. at the HF 732 level of calculation with a 6-31G basis set including ghost 733 atoms (basis set B in Lacivita et al. 2012). 734

Table 1 FF-NR static and dynamic vibrational (nuclear relaxation) contributions to the second hyperpolarizability  $\gamma$  (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)	
	$g^{\mu}$	$\gamma_4^{nr}$	$\overline{g^{lpha}}$	$\gamma_2^{nr}$	$g^{eta}$	$\gamma_1^{nr}$
уууу	$2419 \pm 44$	1169	$1672 \pm 26$	422	$1223 \pm 8$	-27
ZZZZ	$2843 \pm 283$	371	$2780 \pm 16$	308	$2514 \pm 6$	42
xxxy	-	-	-	_	$(1.373 \pm 0.004) \times 10^5$	2900
хууу	_	-	$1675 \pm 80$	5247	$-3614 \pm 5$	-42
ххуу	-	-	$9877 \pm 1009$	$2.332\times10^4$	$(-1.358\pm 0.002)\times 10^4$	-140
xxzz	_	-	$(1.158 \pm 0.241) \times 10^4$	5874	$5766 \pm 7$	60
yyzz	$1541 \pm 17$	933	$861.3 \pm 15.7$	253.2	$658.1 \pm 3.1$	50
zzyy	= yyzz	= yyzz	$671.7 \pm 7.3$	63.7	$602.6 \pm 0.9$	-5.5
yzyz	= yyzz	= yyzz	$1855 \pm 31$	1247	= yyzz	= yyzz
xyzz	_	-	$879.4 \pm 202.8$	659.5	$250.2 \pm 1.9$	30.3
xzyz	-	-	$2740 \pm 86$	2520	= xyzz	= xyzz
xzzy	-	-	= xzyz	= xzyz	$220.0\pm0.1$	0.1

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

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

#### 3.2 KDP and urea: dielectric tensor $e^{e}$ , 744 second-harmonic generation d<sup>e</sup>, and the effect 745 of the field wavelength $\lambda$ 746

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

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

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

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

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

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

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

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

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

801

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

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

	TIE	DDE0	DALVD	DDE	IDA	
	HF	PBE0	B3LYP	PBE	LDA	Exp.
$\epsilon^{e}_{xx}$	2.025	2.223	2.230	2.328	2.340	2.23 <sup>a</sup>
	(1.712)	(2.195)	(2.244)	(2.526)	(2.562)	
$\epsilon^{e}_{zz}$	1.868	2.039	2.046	2.132	2.159	2.13 <sup>a</sup>
	(1.639)	(2.043)	(2.086)	(2.317)	(2.369)	
$d^e_{xyz}$	0.197	0.355	0.373	0.467	0.488	0.38 <sup>b</sup>
	(0.066)	(0.302)	(0.341)	(0.609)	(0.647)	
$E_g$	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

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

	$\lambda$ (nm)		HF	PBE0	B3LYP	LC-BLYP	PBE	LDA	Exp.
Urea	8	$\epsilon^{e}_{xx}$	1.901	2.059	2.070	2.057	2.149	2.186	
		$\epsilon^{e}_{_{77}}$	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
		$\epsilon^{e}_{_{77}}$	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
		$\epsilon^{e}_{_{77}}$	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	
		$\epsilon^{e}_{_{77}}$	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
		$\epsilon^{e}_{_{77}}$	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
		$\epsilon^{e}_{zz}$	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,  $e_{zz}^e$ , 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).

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

A few comments concerning  $\epsilon^{e}$ :

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

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

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

The data shown in Table 2 are static, but they refer to elec-842 tronic calculations or measurements in which a high (UV-vis-843 ible) field frequency has been used. In Table 3, we explore, for 844 both urea and KDP, the effect of the field wavelength, for the 845 electronic dielectric tensor (Rérat et al. 2015). Computed SHG 846 results for urea and KDP (see Table 4) show that B3LYP 847 reproduces rather well the experimental values measured at 848 1064 and 600 nm. For urea, the quasi-isotropic electronic con-849 tribution is slightly smaller than the experimental value at 850  $\lambda = 1064$  nm (Halbout et al. 1979). At this wavelength, the 851 vibrational contribution may not be completely negligible. For 852 that reason, the double harmonic vibrational  $d_{xy7(xy)}^{nr}(-2\omega;\omega,\omega)$ 853 components were calculated at  $\lambda = 1064$  nm (see Eq. 6 in 854 Rérat et al. 2015); their value is 0.041 (0.035) pm V<sup>-1</sup> for 855 B3LYP, and has the same sign as the electronic contribution 856  $d^{e}_{xyz(zxy)}(-2\omega;\omega,\omega)$ . The total B3LYP  $d^{e+nr}_{xyz(zxy)}$  value is, then, 857 equal to 1.027 and 1.018 pm  $V^{-1}$  which falls essentially at the 858 outer limit of the error bars for the experimental value: 859  $d_{14} = 1.2 \pm 0.1 \text{ pm V}^{-1}$  of Halbout et al. (1979)  $(d_{vvz}^{e+nr} \approx d_{zvv}^{e+nr})$ 860 for wavelength larger than 600 nm). Vibrational anharmonicity 861 and/or temperature effects, which would increase the magni-862 tude of this term, could be among the reasons of the small 863 discrepancy. At 600 nm, the calculated vibrational contribution 864 is four times smaller than at 1064 nm and, thus, can be 865 neglected. The B3LYP value  $(1.371 \text{ and } 1.361 \text{ pm V}^{-1})$  in this 866 case is well within the experimental window:  $1.3 \pm 0.3$  pm V<sup>-1</sup> 867 of Bäuerle et al. (1977). Finally, for KDP, the B3LYP elec-868 tronic value of  $0.41 \text{ pm V}^{-1}$  is in perfect agreement with the 869 available experimental reference, i.e.,  $0.41 \text{ pm V}^{-1}$  (Singh 870 1986). Again, Table 4 clearly shows the well-known tendency 871 of LDA and GGA functionals to grossly overestimate high-872 order electric susceptibilities as the value of the wavelength 873 approaches the resonance. It is noteworthy that  $d_{xyz}^e$  increases 874 at each frequency when the percentage of HF exchange 875

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

	$\lambda$ (nm)		HF	PBE0	B3LYP	LC-BLYP	PBE	LDA	Exp.
Urea	8	$d^e_{xyz}$	0.680	0.823	0.863	0.876	0.949	1.106	
		$d^e_{zxy}$	0.680	0.823	0.863	0.876	0.949	1.106	
	1064	$d_{rvz}^e$	0.738	0.936	0.986	0.989	1.131	1.333	1.2 <u>+</u> 0.1
		$d_{zyy}^{e}$	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 <u>+</u> 0.3
		$d^e_{zyy}$	0.889	1.263	1.361	1.323	1.793	2.191	
KDP	$\infty$	$d_{rvz}^{e}$	0.198	0.354	0.373	0.342	0.467	0.487	
		$d_{zyy}^{e}$	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
		$d^e_{zyy}$	0.207	0.378	0.396	0.363	0.504	0.529	
	600	$d_{rvz}^{e}$	0.228	0.438	0.464	0.416	0.607	0.642	
		$d_{zyy}^{e}$	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)

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

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

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

888 889

The refractive index and birefringence are directly related by 890 simple equations to the components of the dielectric tensor, 891 as shown in Sect. 2.2. 892 893

Here, we will focus on three aspects:

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

As discussed previously, the relative importance of the elec-904 tronic  $\alpha^e$  (Eq. 10) and ionic  $\alpha^{nr}$  (Eq. 12) contributions to 905 polarizability depends on the frequency. In the UV-visible 906 region, the electronic contribution is much larger than the 907 ionic one. Therefore, we will first consider results obtained 908 at the sodium source wavelength,  $\lambda_D = 589.3$  nm, taking into 909 account the electronic contribution alone. 910

A large set of minerals, namely fluorite  $(CaF_2)$ , periclase 911 (MgO), corundum ( $Al_2O_3$ ), quartz ( $SiO_2$ ), rutile ( $TiO_2$ ), 912 anatase (TiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), aragonite (CaCO<sub>3</sub>), anda-913 lusite, sillimanite, and kyanite (three Al<sub>2</sub>SiO<sub>5</sub> polymorphs), 914 forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), topaz (Al<sub>2</sub>SiO<sub>4</sub> $F_2$ ), and perovskite 915 (CaTiO<sub>3</sub>), plus CaO have been selected to cover a large 916 range of refractive index and birefringence values. Table 5 917 reports data calculated for this set of systems, using the 918 B3LYP hybrid functional, relatively severe computational 919

Table 5	Calculated and	experimental	refractive	indices	both at	$(\lambda_{\rm D})$	for	various	minerals	charac	terized	by (	different	symmet	ry
		1				× 11/						~		2	~

				Exp	erimental d	ata	Calculated data					
	Ml	CS	n <sub>X</sub>	$n_Y$	nZ	δ	$2V_Z$	n <sub>X</sub>	$n_Y$	nZ	δ	$2V_Z$
	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	
ſ	Ru	Tet		2.613	2.900	+.287			2.5773	2.8447	+.2674	
Ì	Ana	Tet	2.4889		2.5621	0732		2.4189		2.5147	0958	
ì	Cal	Rho	1.486		1.658	172		1.4796		1.6393	1597	
ĺ	Ara	Ort	1.530	1.681	1.685	155	162.0	1.5245	1.6754	1.6805	1560	160.7
ľ	And	Ort	1.6327	1.6387	1.6439	0112	94.4	1.6180	1.6254	1.6287	0107	112.8
Ł	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
(	Тор	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
Ì	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. (2013). In all but two cases, the experimental geometry has 921 been used. The refractive indices obtained at the optimized 922 geometry are extremely close to the ones computed at the 923 experimental geometry, the exceptions being topaz and 924 perovskite, for which both data are reported in the table. 925 Figure 3 shows the birefringence ( $\delta$ ) as a function of the 926 refringence expressed by the proxy  $\tilde{n}$ . In general, being the 927 birefringence a small fraction of the refractive indices, the 928 intermediate refractive index is a good approximation of 929 the refringence. Therefore,  $\tilde{n} = n_{\gamma}$ ,  $\tilde{n} = n_{\omega}$ , and  $\tilde{n} = n$  for 930 biaxial, uniaxial, and cubic crystals, respectively. 931

Consider first the cubic systems, on the zero axis. For fluorite and CaO, simulation and experiment coincide, whereas, for periclase, the experimental value is slightly larger (1.735 vs 1.725). This is always the case for all systems: when the two circles do not overlap, the experimental  $\tilde{n}$  value is always slightly larger than the computed one, the difference being of the order of 2–3%.

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

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

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

The comparison of calculated and experimental optical 959 sign and angle is more delicate. Figure 3 confirms that for 960 uniaxial crystals, the optical sign is correctly predicted, also 961 for quartz or corundum which are characterized by a small 962 birefringence. For corundum, the discrepancy is the largest 963 in the set; note, however, that the experimental birefringence 964 is the smallest in the set. This indicates that the evaluation 965 of the optical sign of weakly birefringent uniaxial crystals 966 is delicate. 967

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

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Journal : Large 12210	Article No : 931	Pages : 17	MS Code : 931	Dispatch : 20-7-2020
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![](_page_15_Figure_0.jpeg)

**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

geometry. However, the sign of the calculated indicatrixreverses according to the considered geometry.

We mention here also the CaTiO<sub>3</sub> perovskite case, whose 978 crystals are finely twinned. We are not aware of any experi-979 mental determination of the refractive indices, as Table 5 980 981 shows. We found, however, a single experimental determination of the birefringence (El-mallah et al. 1987). We indicate 982 this situation with an ellipse, rather than with a circle. The  $\delta$ 983 value computed at the experimental geometry is quite close 984 to the experimental value (0.019 vs 0.018), whereas the 985 value at the optimized geometry is slightly larger (0.030). 986

A few words now concern the optical angle 2V, shown in Table 5, for which we consider again topaz and perovskite. In both cases, the calculated refractive indices at the two geometries are quite close, but the optical angles are different, and strongly dependent on these small differences. The reason is that the size of the indicatrix depends on the refractive index values, whereas the shape is mainly

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

M1	$\lambda_D$		$\lambda_{ m max}$	$\lambda_{ m max}$				
	Calc.	Exp.	Calc.	Exp.	$\lambda_{\max}$			
Flu	1.4325	1.4336	1.3001	1.3076	9724.0 <sup>a</sup>			
Cor	$1.7442^{\omega}$	1.7673	1.5597	1.5864	5577.0 <sup>b</sup>			
	$1.7326^{\epsilon}$	1.7598	$1.5541^{e}$					
Per	1.7249	1.7355	1.6100	1.6240	5350.0 <sup>c</sup>			
Cal	$1.6392^{\omega}$	1.658	1.6057	1.6210	2170.0 <sup>d</sup>			
	$1.4796^{\epsilon}$	1.486	1.4656	1.4739	2324.0 <sup>d</sup>			
Qtz	$1.5304^{\omega}$	1.5441	1.5027	1.5201	2053.1 <sup>d</sup>			
	$1.5365^{e}$	1.553	1.5103	1.5282	2053.1 <sup>d</sup>			
Ru	$2.5773^{\omega}$	2.613	2.4112	2.451	1529.6 <sup>e</sup>			
	2.8447 <sup>¢</sup>	2.900	2.6501	2.709	1529.6 <sup>e</sup>			

 $\lambda_{\max}$  in nm in the last column. For uniaxial minerals, superscripts  $\omega$  and  $\epsilon$  underline that the lines report  $n_{\omega}$  and  $n_{\epsilon}$ , respectively

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

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

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

dGhosh (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 materials 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  $(n_{\lambda \to \infty}^e)$ , 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 ( $\lambda < 600$  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 absorption spectra ( $\lambda \in [200 - 10,000]$  nm). Available 1020 data are represented in Fig. 4. Table 6 reports the largest wavelength ( $\lambda_{max}$ ) at which the refractive index of the 1022

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![](_page_16_Figure_1.jpeg)

**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  $n_{\lambda\to\infty}^e$  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

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

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

The relative  $\alpha^e$  and  $\alpha^{e+nr}$  contributions to the refractive 1050 index in the various spectral regions can be appreciated from 1051 Fig. 4 where experimental dispersion data and calculated 1052  $n_{\lambda_D}$ ,  $n_{\lambda \to \infty}^e$  and  $n_{\lambda_{\max}}^{e+nr}$  are reported for the materials considered. 1053 As anticipated above, the electronic contribution yields a 1054 fairly good value of the index  $n_{\lambda_D}$  (large open symbols in the 1055 grey vertical strip). However,  $n_{\lambda \to \infty}^{e^{-1}}$  (horizontal lines) deviate 1056 significantly from indices measured at  $\lambda > 4000$  nm. In fact, 1057 this "limit" depends on materials. From our data, a better 1058 provisional "limit" should be 2500 nm. Above 4000 (or 1059 2500) nm, the ionic contribution cannot be neglected and 1060 brings the calculated indices  $(n_{\lambda_{\max}}^{e+nr})$  in very good agreement 1061 with experimental indices. 1062

# 4 Conclusions

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 nowa-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 of constants defining the tensor are obtained with a single calculation, whereas many experiments must be performed for obtaining the same result.

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

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

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

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

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Journal : Large 12210 Articl	icle No : 931 Pages	es : 17 M	AS Code : 931	Dispatch : 20-7-2020
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