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Direct Piezoelectric Tensor of 3D Periodic Systems through a Coupled Perturbed Hartree–Fock/Kohn–Sham Method

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Abstract: A quasi-analytical theoretical method is devised, and implemented in the CRYSTAL program, for calculation of the direct “proper” piezoelectric tensor of periodic systems including both the clamped-nuclei electronic and nuclear relaxation contributions. It is based on using the analytical Coupled-Perturbed-Hartree–Fock/Kohn–Sham (CPHF/KS) procedure to obtain dipole derivatives with respect to lattice deformations as well as internal coordinates. The sole numerical step required involves building the Hessian matrix through differentiation of analytical energy gradients. Two prototypical piezoelectric, non-ferroelectric, crystals, namely ZnO and α -quartz, are used to demonstrate the accuracy and computational efficiency of our new scheme, which significantly improves upon the commonly used numerical Berry phase approach.

Keywords: Piezoelectricity, Polarization in Solids, CPHF, CRYSTAL Program.

Dedicated to Professor Michael Springborg on the occasion of his 60th birthday

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1 Introduction

The phenomenon of piezoelectricity, i.e. the electric polarization (or dipole moment) that arises in certain solid materials as a response to an applied mechanical force, has been known since the late 19th century [1]. However, it is only within the past 20 years, or so, that a thorough microscopic understanding of electric polarization for periodic systems, which is our interest here, has been attained and meaningful *ab initio* calculations of piezoelectricity, as well as its converse (the mechanical strain induced by an applied field) [2–4], have become possible. We now know that, although the electronic polarization may be regarded as a bulk property, it is multivalued depending upon the surface charge [5, 6]. In order to obtain a unique value for the piezoelectricity (sometimes called the “proper” piezoelectric response) one must evaluate/measure this property in terms of a voltage rather than an electric field [5–8]. It is also now recognized that the nuclear relaxation contribution to piezoelectricity due to internal microscopic strain is generally comparable to, or even larger than, the purely electronic (clamped-nuclei) term [9, 10].

Given a satisfactory formalism for periodic systems (see Section 2), the remaining task is to develop an optimum computational algorithm with regard to accuracy and efficiency. On both grounds it is generally preferable to maximize the amount of analytical (versus numerical) differentiation occurring in the calculations. Recently, some of us have formulated, and implemented in the CRYSTAL code [11], a fully analytical method for computing Born charges [12, 13]. This procedure is based on an analytical coupled perturbed Hartree–Fock/Kohn–Sham (CPHF/KS) treatment of the polarization along with analytical gradients of the field-dependent energy. As far as the clamped-nuclei contribution is concerned, the required polarization derivatives with respect to the external strain are evaluated through an extension of the CPHF/KS treatment utilized for the Born charges.

In our evaluation of piezoelectric coefficients the so-called ionic contribution is, by far, the most costly part of the calculation due to the number of derivatives involved. What one requires are the clamped-nuclei (zero strain) derivatives of the polarization with respect to internal coordinates (i.e. the Born charges) and the derivatives of these internal coordinates with respect to the external strain variables. The latter, in turn, are obtained through the Hessian matrix. In this paper the previous analytical calculation of Born charges is utilized in conjunction with a Hessian matrix that is obtained by numerical differentiation of analytical gradients with respect to atomic coordinates and lattice vector components [14–17]. Thus, our treatment of the ionic contribution is quasi-analytical. For a fully analytical procedure the second derivatives should be obtained analytically as well.

Despite some techniques based on density-functional perturbation theory, proposed in the last two decades [18–20], the current most widely used approach to compute the piezoelectric response of crystals is the numerical Berry phase scheme [5, 21, 22]. The latter was first implemented in the CRYSTAL code ten years ago [23, 24] and has been fully automated in CRYSTAL14 [25, 26]. In these previous implementations, the derivatives of the internal coordinates with respect to external strain variables, needed for the ionic contribution, were found by optimization of the internal structure at various strained geometries [25, 27–32]. For good accuracy, such optimizations require very tight convergence, which implies relatively long computation times. The advantages of using numerical differentiation of analytical gradients instead are also documented in this paper.

The outline of our paper is as follows. Section 2 is devoted to our computational strategy. The definition of the clamped-nuclei electronic and nuclear relaxation contributions to the piezoelectric tensor is provided in Section 2.1; the formulation of the analytical CPHF/KS scheme for calculation of both contributions to the “proper” piezoelectric tensor is developed in Section 2.2; Voigt’s notation is introduced in Section 2.3; and the main features of the standard Berry phase approach are briefly recalled in Section 2.4. Then the accuracy and computational efficiency of our method is documented in Section 3, where it is also compared with the Berry phase approach, using ZnO and α -quartz as test cases. Finally, our conclusions are presented in Section 4.

2 Computational strategy

2.1 Definition of the piezoelectric tensor

The total “proper” direct piezoelectric response of a crystal can be represented by a third-rank tensor and is given by the sum of an electronic and a nuclear term, $\mathbf{e} = \mathbf{e}^{\text{ele}} + \mathbf{e}^{\text{nuc}}$. The electronic term measures the variation of the current density \mathbf{J} with strain when no nuclear relaxation is allowed (clamped-nuclei condition; $u = 0$) [5]:

$$e_{ijk}^{\text{ele}} = \left. \frac{\partial J_i}{\partial \epsilon_{jk}} \right|_{u=0} = \sum_{\alpha} \left. \frac{\partial J_i}{\partial a_{\alpha j}} a_{\alpha k} \right|_{u=0}. \quad (1)$$

Here i, j, k are Cartesian indices, ϵ is the symmetric second-rank pure strain tensor and the $a_{\alpha k}$ are Cartesian components of the three lattice vectors \mathbf{a}_{α} , $\alpha = 1, 2, 3$. The second equality in Equation (1) arises from the expression for the effect of an

elastic deformation on the lattice parameters, i.e. [33]

$$a'_{\alpha j} = \sum_k (\delta_{jk} + \epsilon_{jk}) a_{\alpha k}, \quad (2)$$

in which δ_{jk} is the Kronecker delta.

The nuclear relaxation contribution can be expressed as [9]:

$$e_{ijk}^{\text{nuc}} = \frac{1}{V} \sum_s Z_{is}^* \frac{du_s}{d\epsilon_{jk}}, \quad (3)$$

where $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the cell volume, the u_s are $3N - 3$ fractional coordinates (N being the number of atoms per cell) obtained from the $3N$ atomic fractional coordinates by orthogonalization to the three translations along \hat{x} , \hat{y} and \hat{z} , and \mathbf{Z}^* is the Born atomic charge tensor defined in terms of the resulting set of fractional atomic coordinates:

$$Z_{is}^* = \frac{\partial^2 E^{\text{TOT}}}{\partial \mathcal{E}_i \partial u_s}. \quad (4)$$

In the latter relation \mathcal{E}_i is a Cartesian component of the applied electric field and E^{TOT} the total energy of the system (to be given an explicit expression below).

2.2 The coupled-perturbed approach

2.2.1 Electronic Term

The electronic contribution to the “proper” piezoelectric tensor defined in Equation (1) can be expressed in terms of the total polarization \mathbf{P} as [5]:

$$e_{ijk}^{\text{ele}} = \left. \frac{\partial J_i}{\partial \epsilon_{jk}} \right|_{u=0} = \left. \frac{\partial P_i}{\partial \epsilon_{jk}} \right|_{u=0} + P_i \delta_{jk} - P_k \delta_{ij}, \quad (5)$$

where the first term on the right-hand-side can be understood as the electronic contribution to the “improper” piezoelectric tensor. By expressing the polarization in terms of total energy derivatives, and by exploiting the second equality in Equation (1), one gets:

$$\left. \frac{\partial J_i}{\partial \epsilon_{jk}} \right|_{u=0} = \frac{1}{V} \sum_{\alpha} a_{\alpha k} \left. \frac{\partial^2 E^{\text{TOT}}}{\partial \mathcal{E}_i \partial a_{\alpha j}} \right|_{u=0} - P_k \delta_{ij}. \quad (6)$$

The second derivatives in the term on the rhs of Equation (6) are the same as the components of the Born charge tensor in (4) except that differentiation with respect to internal atomic positions has been replaced by differentiation with respect to the lattice parameters. Here we develop an expression for the latter by

extending the analytical CPHF/KS approach recently presented for calculation of the Born tensor by Maschio, Kirtman, Orlando and Rérat (MKOR) [12]. Extensive reference will also be made to the work by Doll, Dovesi and Orlando (DDO) on the development, and implementation in the CRYSTAL program, of analytical energy gradients with respect to lattice distortions [16].

We start with the Hartree–Fock expression (the extension to Kohn–Sham DFT can be found in MKOR) for the total energy of a periodic system in the presence of an electric field:

$$E^{TOT} = \text{Tr} \left(\left[H + \frac{1}{2}(B + T + Sq) + \sum_l \varepsilon_l \Omega_l \right] D \right) + E^{\text{nuc}} + \sum_{l,m,A} \varepsilon_l \zeta_A \mathcal{R}_m^A \delta_{lm}. \quad (7)$$

In this expression Tr signifies the trace and H , B , T , S , Ω_l and D are direct space matrices in an atomic orbital (AO) representation. Specifically, H is the core Hamiltonian, S the overlap, B the electron–electron interaction term (which involves evaluation of two-electron integrals), and T the Ewald infinite summation contribution to the electron–electron interaction (which depends upon the density matrix D). Furthermore, $\mathcal{R}_m^A = \sum_\beta f_{A,\beta} a_{\beta m}$ is the position of atom A along the Cartesian direction m with fractional coordinate $f_{A,\beta}$, ζ_A is the nuclear charge of atom A and E^{nuc} the nuclear-nuclear interaction energy.

Two quantities, Ω_l and q , in Equation (7) require a more detailed explanation. Ω_l is the AO matrix representation, in direct space, for the l Cartesian component of an operator, $\hat{\Omega}(\mathbf{k})$, which determines the interaction of the electrons with the external electric field. For an infinite periodic system it is defined as [34–38]:

$$\hat{\Omega}(\mathbf{k}) = i e^{i\mathbf{k}\cdot\mathbf{r}} \nabla_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}}. \quad (8)$$

The properties of this matrix, which is central to our approach, have been extensively discussed in previous papers by some of us [12, 39, 40]. If the matrix of crystalline orbital eigenvectors $C(\mathbf{k})$ is expanded as a Taylor series in the field components:

$$C(\mathbf{k}) = C^{(0)}(\mathbf{k}) + \sum_l \varepsilon_l C^{(\varepsilon_l)}(\mathbf{k}) + \sum_{l,m} \varepsilon_l \varepsilon_m C^{(\varepsilon_l, \varepsilon_m)}(\mathbf{k}) + \dots \quad (9)$$

then, the zeroth-order matrix representation of the operator (8) may be written as [12]:

$$\Omega_l^{(0)}(\mathbf{k}) = M_l(\mathbf{k}) + iS(\mathbf{k})C^{(0)}(\mathbf{k})Q_l(\mathbf{k})C^{(0)\dagger}(\mathbf{k})S(\mathbf{k}), \quad (10)$$

where $M_l(\mathbf{k}) = \Xi_l(\mathbf{k}) + iS^{(k_l)}(\mathbf{k})$. Here $\Xi_l(\mathbf{k})$ is the matrix representing the component of the electron position coordinate along l and $S^{(k_l)}(\mathbf{k})$ is the derivative of the AO overlap matrix $S(\mathbf{k})$ with respect to the wave vector component k_l [41]. The crystal orbital (CO) matrix $Q_l(\mathbf{k})$ is defined by:

$$\frac{\partial}{\partial k_l} C^{(0)}(\mathbf{k}) = C^{(0)}(\mathbf{k}) Q_l(\mathbf{k}). \quad (11)$$

Note that this CO matrix contains both real and imaginary parts. It has been shown previously that the imaginary diagonal components, which contribute to the dipole moment, are only determined up to an integer multiple of the unit cell length along each of the crystal axes [38, 42, 43].

In Equation (7), q is the (scalar) value of the spheropole. The spheropole term arises only in 3D periodic systems. It occurs because the charge distribution is approximated by a model in the long range and it is needed in order to guarantee that the average of the electrostatic potential vanishes [44]. We note that q depends upon the density matrix, $q = \text{Tr}(D\Omega)$, where Ω is the matrix of spheropolar integrals whose explicit form can be found elsewhere [16, 44].

Following the scheme of the MKOR treatment, it is convenient to begin with the expression for the analytical gradient of E^{TOT} with respect to cell parameters (see Equation (6) in DDO) and, then, differentiate this expression with respect to the electric field:

$$\begin{aligned} \left. \frac{\partial E^{TOT}}{\partial a_{\alpha j}} \right|_{a^0} &= \left. \frac{\partial E^{\text{nuc}}}{\partial a_{\alpha j}} \right|_{a^0} + \text{Tr} \left(\left[\frac{1}{2} (\mathfrak{B}^{(a_{\alpha j})} + \mathfrak{T}^{(a_{\alpha j})} + q^{(a_{\alpha j})} S + q S^{(a_{\alpha j})}) \right. \right. \\ &\quad \left. \left. + \sum_l \mathcal{E}_l \Omega_l^{(a_{\alpha j})} + H^{(a_{\alpha j})} \right] D - S^{(a_{\alpha j})} D_W \right)_{a^0} \\ &\quad + \sum_{A,l} \mathcal{E}_l \delta_{lj} \zeta_A f_{A,\alpha} \end{aligned} \quad (12)$$

The subscript a^0 here indicates that the quantity in question is evaluated for equilibrium cell parameters. As customary in the evaluation of energy gradients [45], the eigenvalue-weighted density matrix D_W has been introduced in order to avoid calculating derivatives of the CO coefficients.

In Equation (12) the first term on the rhs is not trivial to evaluate. However, it does not depend on the electric field and is, therefore, not relevant for the present discussion. The derivatives that appear in the second term can be treated, for the most part, in almost exactly the same way as those that occur for the Born tensor in MKOR except that now the lattice parameters are varied with the internal vibrational displacements held fixed rather than the other way around. In particular, $\mathfrak{B}^{(a_{\alpha j})}$, $\mathfrak{T}^{(a_{\alpha j})}$ and $q^{(a_{\alpha j})}$ are derivatives of the electron-electron interaction and

spheropole terms B , T and q , taken by keeping the density matrix constant; they correspond to Equations (30)–(32) in MKOR. That leaves $H^{(a_{\alpha j})}$, the derivative of the kinetic energy and electron-nuclear interaction contributions, as well as $S^{(a_{\alpha j})}$, neither of which contain the density matrix.

There are three terms that require further elaboration. One of them is the spheropole derivative $q^{(a_{\alpha j})}$, which contains an additional term with respect to the Born tensor case (see Equation (48) of DDO):

$$q^{(a_{\alpha j})} = \text{Tr} \left(DQ^{(a_{\alpha j})} \right) + \frac{q}{V} \frac{\partial V}{\partial a_{\alpha j}}. \quad (13)$$

The others are the two terms in Equation (12) that depend explicitly on the field. At variance with the Born tensor, when the lattice parameters are varied these two terms do not yield a unique value for the derivative. The last term in Equation (12) describes the interaction between the external field and the nuclear charges, whereas the interaction of the electrons with the external field is given by $\sum_l \mathcal{E}_l \Omega_l^{(a_{\alpha j})}$. Each of these terms, individually, depends upon the choice of the origin and the unit cell, which leads to different possible values depending upon the surface termination of the lattice of point charges [5]. However, this dependence cancels except for a contribution that arises from the diagonal imaginary elements of Q_l [7, 38]:

$$\frac{1}{2n_k} \sum_{\mathbf{k}} \text{Tr} \left(i \left(Q_l^{(a_{\alpha j})}(\mathbf{k}) - Q_l^{(a_{\alpha j})\dagger}(\mathbf{k}) \right) n \right)_{a^0} = e \delta_{ij} N_{\alpha}, \quad (14)$$

where n is the diagonal occupation number matrix with eigenvalues equal to 0 for virtual orbitals and 1 (or 2 in closed shell systems) for occupied orbitals, n_k is the number of \mathbf{k} -points included in the summation, e is the magnitude of the electron charge and N_{α} is an arbitrary integer (or even integer for closed-shell systems). Apart from normalization, the term on the lhs here is the same as in Equation (39) of MKOR except, again, that the derivatives are with respect to external strain rather than internal atomic displacements. An alternative derivation is given in Reference [13]. Physically, this term accounts for the dipole moment generated by transfer of a quantized number of charges, N_{α} , per unit cell between opposite surfaces [5, 6]. However, we note that the polarization P_l also contains a contribution $\sum_{\beta} e N_{\beta} a_{\beta l}$ due to the charge transfer. Indeed, when the “proper” piezoelectric tensor, the subject of this paper, is determined by subtracting out $P_k \delta_{ij}$ (see Equation 6) the charge transfer terms cancel out. On the contrary, such cancellation does not occur for the “improper” piezoelectric tensor, which is given by the first term on the rhs of Equation (5) and is also physically observable, as discussed elsewhere for one-dimensional periodic systems [6].

By differentiating Equation (12) with respect to the electric field we obtain the analogue of Equation (48) in MKOR:

$$\begin{aligned} \left. \frac{\partial}{\partial \mathcal{E}_i} \frac{\partial E^{TOT}}{\partial a_{\alpha j}} \right|_{\mathcal{E}=0, a^0} &= \text{Tr} \left(\left[H^{(a_{\alpha j})} + \mathfrak{B}^{(a_{\alpha j})} + \frac{1}{2} \mathfrak{T}^{(a_{\alpha j})} \right] D^{(\mathcal{E}_i)} \right. \\ &+ \left[\frac{1}{2} \left(q^{(a_{\alpha j})} S + \mathfrak{T}^{(a_{\alpha j})} \right)^{(\mathcal{E}_i)} + \overline{M}_i^{(a_{\alpha j})} \right] D^{(0)} - S^{(a_{\alpha i})} D''_W^{(\mathcal{E}_i)} \Big|_{a^0} \\ &+ \sum_A \zeta_A f_{A,\alpha} \delta_{ij} + e \delta_{ij} N_\alpha, \end{aligned} \quad (15)$$

where $D''_W^{(\mathcal{E}_i)}$ is a modified form of the electric field derivative of the eigenvalue-weighted density matrix (see Equation 45 of MKOR). The modification, indicated by the $''$ superscript, entails subtracting out the terms containing Q from the Lagrange multiplier matrix that appears in D'' . Following through on the terms singled out in connection with Equation (12), we note that the spheropole term becomes (see Equation 13):

$$\left(q^{(a_{\alpha j})} \right)^{(\mathcal{E}_i)} = \text{Tr} \left(D Q^{(a_{\alpha j})} \right)^{(\mathcal{E}_i)} + \frac{q^{(\mathcal{E}_i)}}{V} \frac{\partial V}{\partial a_{\alpha j}}. \quad (16)$$

In addition, the two terms on the rhs that arise from Ω_i in Equation (12), namely $\overline{M}_i^{(a_{\alpha j})} D^{(0)}$ (\overline{M}_i is the hermitized version of M_i) and $\delta_{ij} N_\alpha$, as well as the nuclear contribution to the dipole moment (next to last term on rhs of Equation 15) all depend upon the origin and shape of the lattice cell. However, this dependence does not occur in the “proper” piezoelectric effect since, after the sum is taken, what remains is canceled by the $-P_k \delta_{ij}$ term in Equation (6).

2.2.2 Nuclear relaxation term

The nuclear relaxation contribution to the “proper” piezoelectricity is given by Equation (3). In fact, there is no distinction between “proper” and “improper” for this term because the atomic Born charge tensor \mathbf{Z}^* is independent of surface charges as noted in MKOR. In the present approach \mathbf{Z}^* is computed analytically through a CPHF/KS strategy [12, 13], and is obtained in conjunction with the determination of the clamped-nuclei electronic term. That leaves the $du_s/d\epsilon_{jk}$ derivatives in Equation (3). They can be obtained in either of two ways: i) optimization of the internal geometry at strained configurations or ii) from the full Hessian matrix \mathbf{H} of energy second derivatives with respect to both fractional atomic displacements and lattice deformations (with a truncation to quadratic terms in the Taylor’s expansion of the energy) [20]. We have found that ii) is preferable, as will be

documented in Section 3.2. In that procedure the following relation is utilized:

$$\frac{du_s}{d\epsilon_{jk}} = - \sum_{s'=1}^{3N-3} H_{jk,s'} \times (H^{-1})_{s's}, \quad (17)$$

in which

$$H_{jk,s'} = \left(\frac{\partial^2 E}{\partial \epsilon_{jk} \partial u_{s'}} \right), \quad (18)$$

and $(H^{-1})_{s's}$ is an element of the inverse of the atomic Hessian:

$$H_{s's} = \left(\frac{\partial^2 E}{\partial u_{s'} \partial u_s} \right). \quad (19)$$

In the present implementation, the elements of the Hessian matrix are computed as numerical derivatives of analytical energy gradients. Either a two-point or three-point formula is employed in obtaining the numerical derivatives with the analytical gradients computed at the equilibrium configuration and at one or two non-equilibrium, i.e. displaced or strained, configurations for Equations (19) and (18), respectively. As both the $3N - 3$ fractional atomic coordinates s and the 6 symmetry-independent lattice deformations ϵ_{jk} (the pure strain tensor ϵ being symmetric) imply global atomic displacements, non-equilibrium configurations are defined in terms of the largest induced Cartesian atomic displacement δ (by default $\delta = 0.004$ bohr). If mass-weighted coordinates are used instead of u_s , then by diagonalizing the atomic Hessian matrix (Equation (19)), the total nuclear response e^{nuc} can be expressed as a sum of normal mode-specific contributions:

$$e_{ijk}^{\text{nuc}} = -\frac{1}{V} \sum_p Z_{ip}^* \frac{H_{jk,p}}{\omega_p^2}, \quad (20)$$

where $p = 1, \dots, 3N - 3$ labels each vibration normal mode and ν_p is the corresponding vibration frequency.

2.3 Voigt's notation

As the pure strain ϵ is a symmetric second-rank tensor, there are six independent components ϵ_{jk} . It is convenient to adopt Voigt's notation, which maps the two Cartesian index notation (jk) into a one index notation (v) , where $v = 1 \equiv xx$, $v = 2 \equiv yy$, $v = 3 \equiv zz$, $v = 4 \equiv yz$, $v = 5 \equiv xz$, and $v = 6 \equiv xy$ [46]. Accordingly, the third-rank direct piezoelectric tensor can be represented as a two-index quantity:

$$e_{ijk} \rightarrow e_{iv}. \quad (21)$$

Voigt's notation will be used in the rest of the manuscript.

2.4 The Berry phase approach

Within the modern theory of polarization [5, 21, 22], the direct “proper” piezoelectric constants of 3D crystals can be obtained from derivatives of the numerical Berry phase φ with respect to the strain as:

$$e_{iv} = \frac{e}{2\pi V} \sum_{\alpha} a_{\alpha i} \frac{d\varphi_{\alpha}}{d\epsilon_v}, \quad (22)$$

where φ_{α} represents the Berry phase along the \mathbf{a}_{α} lattice vector. In the fully-automated implementation available in the CRYSTAL14 version of the program, the derivatives in Equation (22) were obtained numerically by finite differences over Berry phases computed at N_p strained configurations, which span a strain amplitude Δ (by default, $N_p = 3$ and $\Delta = \pm 1.5\%$ of the unstrained lattice parameters) [25, 26]. The effect of nuclear relaxation is evaluated numerically by allowing internal coordinates u_s to relax at strained configurations, which corresponds to procedure i) in Section 2.2.2. If geometry optimizations at strained configurations are avoided, the purely electronic contribution is computed, which would correspond to evaluating partial instead of total derivatives in Equation (22).

3 Results and discussion

In this section, we document and discuss the accuracy and efficiency of the analytical scheme (based on the CPHF/KS method) for the quantum-mechanical evaluation of the “proper” direct piezoelectric tensor of crystals. A comparison with the commonly used numerical approach (based on the Berry phase method), as in CRYSTAL14, is also presented in order to demonstrate the computational advantages of the present formulation/implementation. Since the electronic and nuclear relaxation contributions to the total piezoelectric response are computed following distinct computational strategies we shall discuss these terms separately. For this analysis, two prototypical non-ferroelectric piezoelectric materials are considered: hexagonal zinc oxide, ZnO, and trigonal α -quartz, α -SiO₂. The former has three symmetry-independent piezoelectric constants: e_{15} , e_{31} and e_{33} , whereas the latter has two: e_{11} and e_{14} .

For our purposes here it is convenient to use the CPKS treatment with the generalized gradient PBE [47] functional. We have chosen a local basis set of atom-centered Gaussian-type functions with the following contractions: (8s)(64111sp)(41d) for Zn, (8s)(411sp)(1d) for O, and (8s)(841sp)(1d) for Si. A tight threshold of 10^{-10} hartree is set for the energy convergence of the field-free self-consistent-field (SCF) procedure. The convergence threshold T_{α} for the SCF

procedure within the CPKS method will be explicitly discussed in the next sub-sections. In evaluating the long-range electron-electron Coulomb interactions the maximum order of shell multipoles is set to 6 (see `POLEORDR` keyword in the `CRYSTAL14` manual [48]). The exchange-correlation contribution to the Fock matrix is evaluated by numerical integration over the unit cell volume. Radial and angular points of the integration grid were generated by Gauss-Legendre radial quadrature and a Lebedev two-dimensional angular distribution. In the present work, a pruned grid with 99 radial points and a maximum of 1454 angular points is used, which corresponds to the densest grid (see `XXLGRID` keyword in the `CRYSTAL14` manual) [48] among the pre-defined ones. Other computational parameters will be discussed in the following sub-sections.

3.1 Computational parameters for electronic term

We consider, first, the electronic “clamped-nuclei” piezoelectric constants. They are reported in Table 1 as a function of two computational parameters: the shrinking factor S , which determines the number of \mathbf{k} -points sampled in reciprocal space, and the tolerances T_i (i.e. 10^{-T_i}), which govern the truncation of the infinite Coulomb and exchange series. In the `CRYSTAL` program there are five such thresholds that are set here to $T_1 = T_2 = T_3 = T_4 = \frac{1}{2}T_5 = T$ [48].

It is seen in the table that the calculated piezoelectric coefficients of the two crystals are quite insensitive to the values of both computational parameters except for small values of S . In that case, the CP approach is more sensitive than the BP approach for ZnO, whereas the situation is reversed for α -quartz, although the effect is much smaller. Both approaches converge nicely to the same limiting values. For ZnO the analytical CP coefficients are converged to three significant figures at $S = 9$, $T = 9$ while the numerical BP coefficients are fully converged at $S = 12$, $T = 8$. The corresponding parameters for α -quartz are $S = 3$, $T = 5$ for the CP method and $S = 6$, $T = 5$ for the BP method.

We turn now to the algorithm-specific computational parameters. The main computational parameter to explore for the CP analytical strategy is the threshold T_α (i.e. 10^{-T_α}), which controls the convergence of the self-consistent CPKS equations in terms of components of the polarizability tensor α . In the upper part of Table 2, this parameter is considered in the range $10^0 - 10^{-4}$. For both systems, $T_\alpha = 2$ provides converged coefficients to three significant figures. In the BP approach, as recalled in Section 2.4, the piezoelectric constants are determined via numerical derivatives of the Berry phase with respect to the strain. The derivatives are calculated by finite differences with the Berry phases evaluated at N_p equally spaced points with a maximum strain amplitude Δ (the latter is expressed as a percent of

Table 1: The clamped-nuclei electronic contribution to the symmetry-independent piezoelectric constants of ZnO and α -quartz for the Berry phase (BP) and CPKS (CP) approaches as a function of the shrinking factor S and truncation tolerance T of the infinite Coulomb series. All values in units of C/m^2 .

ZnO	S = 3		S = 6		S = 9		S = 12	
	BP	CP	BP	CP	BP	CP	BP	CP
e_{15}^{ele}	0.315	0.391	0.316	0.323	0.318	0.319	0.319	0.319
e_{31}^{ele}	0.309	0.356	0.306	0.309	0.306	0.307	0.307	0.307
e_{33}^{ele}	-0.635	-0.647	-0.619	-0.617	-0.616	-0.615	-0.615	-0.615
	T = 6		T = 7		T = 8		T = 9	
	BP	CP	BP	CP	BP	CP	BP	CP
e_{15}^{ele}	0.319	0.320	0.319	0.320	0.319	0.320	0.319	0.319
e_{31}^{ele}	0.306	0.308	0.307	0.307	0.307	0.307	0.307	0.307
e_{33}^{ele}	-0.614	-0.612	-0.614	-0.613	-0.615	-0.614	-0.615	-0.615
α -SiO ₂	S = 2		S = 3		S = 6		S = 9	
	BP	CP	BP	CP	BP	CP	BP	CP
e_{11}^{ele}	-0.142	-0.147	-0.144	-0.145	-0.145	-0.145	-0.145	-0.145
e_{14}^{ele}	0.068	0.074	0.071	0.073	0.073	0.073	0.073	0.073
	T = 5		T = 6		T = 7		T = 8	
	BP	CP	BP	CP	BP	CP	BP	CP
e_{11}^{ele}	-0.145	-0.145	-0.145	-0.145	-0.145	-0.145	-0.145	-0.145
e_{14}^{ele}	0.073	0.073	0.073	0.073	0.073	0.073	0.073	0.073

the equilibrium lattice parameter). The lower part of Table 2 documents the combined effect of N_p and Δ . Overall, a very satisfactory numerical stability of the computed numerical derivatives is found.

3.2 Computational parameters for nuclear relaxation term

We now proceed to examine the effect of the (algorithm-specific) computational parameters on the nuclear relaxation contribution to the piezoelectric coefficients of ZnO and α -quartz. The computational parameters discussed in Section 3.1 (namely S , T , T_α , N_p and Δ) are kept fixed at values that guarantee full convergence of the clamped-nuclei electronic term in both strategies.

The nuclear relaxation factor $du_s/d\epsilon_v$ in Equation (3) is accounted for differently in the two approaches. Within the BP approach, geometry optimizations are performed at strained lattice configurations through a quasi-Newton scheme [27].

Table 2: Effect of algorithm-specific computational parameters on the clamped-nuclei electronic piezoelectric constants of ZnO and α -quartz. For the CP approach, T_α is the threshold for convergence of the CPKS equations; for the BP approach, Δ is the strain amplitude and N_p is the number of points used to numerically evaluate the Berry phase derivative with respect to strain.

		CP				
	T_α	0	1	2	3	4
ZnO	e_{15}^{ele}	0.320	0.319	0.319	0.319	0.319
	e_{31}^{ele}	0.347	0.322	0.307	0.307	0.307
	e_{33}^{ele}	-0.578	-0.601	-0.615	-0.615	-0.615
α -SiO ₂	e_{11}^{ele}	-0.153	-0.145	-0.145	-0.145	-0.145
	e_{14}^{ele}	0.062	0.074	0.073	0.073	0.073
		BP				
	N_p	3	3	5	5	5
	Δ	$\pm 1\%$	$\pm 1.5\%$	$\pm 1\%$	$\pm 1.5\%$	$\pm 2\%$
ZnO	e_{15}^{ele}	0.319	0.319	0.319	0.319	0.319
	e_{31}^{ele}	0.307	0.307	0.307	0.307	0.307
	e_{33}^{ele}	-0.616	-0.615	-0.614	-0.615	-0.616
α -SiO ₂	e_{11}^{ele}	-0.145	-0.145	-0.145	-0.145	-0.145
	e_{14}^{ele}	0.073	0.073	0.073	0.073	0.073

A threshold parameter T_G (i.e. 10^{-T_G}) is used to determine the convergence of the geometry optimization process based on the root mean square value of the gradients. In the CP approach, the same factor is evaluated though Equation (17) by constructing the Hessian matrix \mathbf{H} from finite differences of analytical gradients evaluated at n_p displaced/distorted configurations with a displacement step δ .

Table 3 documents the effect of the above parameters on computed total (clamped-nuclei electronic plus nuclear relaxation) piezoelectric coefficients of ZnO and α -quartz. At the outset we stress the fact that the nuclear relaxation contribution is dominant in every case so that total values of all piezoelectric coefficients e_{iv} are of opposite sign to the corresponding clamped-nuclei electronic contribution e_{iv}^{ele} reported in previous tables. The T_G threshold used for the BP method is explored in the range $3 \cdot 10^{-4} - 1 \cdot 10^{-5}$. Although the computed coefficients are not dramatically affected by the threshold value, the convergence is very slow. This observation is based on the fact that the third significant figure varies between $T_G = 0.3$ and 0.1 . For α -quartz, in particular, the coefficient values are probably not fully converged. In general, then, tighter values than $1 \cdot 10^{-5}$ might need to be used for T_G , which would require a tightening of many other computa-

Table 3: Effect on the total piezoelectric constants of ZnO and α -quartz of the algorithm-specific computational parameters related to the nuclear relaxation term. For the CP strategy, the number n_p of displaced/deformed configurations and the step δ (in bohr) used in the construction of the Hessian matrix from finite differences of analytical gradients are considered. For the BP strategy, the threshold T_G (in units of 10^{-4} a.u.) controlling the convergence of the geometry optimizations in terms of the root mean square of the gradients is explored.

		CP				
		2	2	3	3	3
	n_p					
	δ	0.004	0.008	0.004	0.006	0.008
ZnO	e_{15}	-0.497	-0.497	-0.497	-0.497	-0.496
	e_{31}	-0.593	-0.598	-0.590	-0.589	-0.589
	e_{33}	1.148	1.147	1.148	1.148	1.148
α -SiO ₂	e_{11}	0.188	0.188	0.190	0.190	0.190
	e_{14}	-0.068	-0.070	-0.067	-0.067	-0.067
		BP				
		3	1	0.6	0.3	0.1
	T_G					
ZnO	e_{15}	-0.490	-0.497	-0.497	-0.498	-0.498
	e_{31}	-0.584	-0.589	-0.589	-0.590	-0.589
	e_{33}	1.146	1.146	1.146	1.149	1.149
α -SiO ₂	e_{11}	0.196	0.195	0.194	0.194	0.193
	e_{14}	-0.062	-0.063	-0.064	-0.064	-0.065

tional parameters (such as the DFT numerical integration grid, the tolerances T_i , etc.) to ensure the necessary numerical accuracy.

With regard to the CP approach, Table 3 shows that the amplitude of the step δ has a very small effect on most piezoelectric coefficients. On the contrary, passing from a two-point formula $n_p = 2$ to a three-point formula $n_p = 3$ in constructing the Hessian leads to a noticeable improvement of the nuclear relaxation term (in particular, for the e_{31} coefficient of ZnO and for both coefficients of α -quartz). When the two overall strategies are compared with each other, small differences in the calculated coefficients are observed. These differences lie within the expected range of round-off error due to the numerical differentiations involved in both the CP and BP procedures.

Table 4: Wall-clock time (in minutes) of the calculation, running in parallel mode on 24 processors, of the electronic clamped-nuclei term of the full piezoelectric tensor of ZnO and α -quartz, as a function of the algorithm-specific computational parameters T_α and N_p for the CP and BP approaches, respectively.

T_α	CP			
	0	1	2	3
ZnO	7.1	7.8	8.7	9.3
α -SiO ₂	7.9	9.8	11.0	12.6

N_p	BP			
	3	5	7	9
ZnO	47	67	88	108
α -SiO ₂	55	83	111	139

3.3 Computational performance

In this section we compare the computational performance (in terms of required wall-clock time) of the two approaches for determining the total direct third-rank piezoelectric tensor of ZnO and α -quartz. Although symmetry can be utilized in both schemes, it has not yet been implemented for the CP procedure. Thus, to enable a fair comparison here, symmetry was not exploited in either case.

Table 4 reports the wall-clock time required to run calculations (in parallel over 24 processors) of the clamped-nuclei electronic term including, as well, the Born charges needed for the nuclear relaxation term. For the clamped-nuclei electronic term there are just two algorithm-specific computational parameters that need to be considered, namely T_α for CP and N_p for BP (the step size Δ does not affect timings). From inspection of the table, a couple of inferences can be made: i) the CP analytical scheme is less costly than the numerical BP one (roughly by a factor of 5 for both crystals if optimal parameters are considered, i.e. $T_\alpha = 2$ and $N_p = 3$); ii) the computational cost only slightly increases for the CP scheme as a function of T_α (increasing by about 31% passing from $T_\alpha = 0$ to $T_\alpha = 3$).

The relative performance of the two schemes for the nuclear relaxation term may be discerned from Table 5, which reports the wall-clock time of the total calculation as well as the difference (in parentheses) between the total time and that required for computation of the clamped-nuclei electronic term. The latter is taken as the time for computation of the nuclear relaxation contribution. Given that within the CP scheme Born charges are computed along with the electronic contribution, the numbers in parentheses for both schemes essentially correspond to the times required to compute $du_s/d\epsilon_{jk}$. From the table we see that: i) Compu-

Table 5: Wall-clock time (minutes), when running in parallel mode on 24 processors, for calculation of the total (clamped-nuclei electronic plus nuclear relaxation) piezoelectric tensor of ZnO and α -quartz. Values are reported as a function of the algorithm-specific computational parameters n_p and T_G for the CP and BP approaches, respectively. In parentheses, the difference between the wall-clock time of a total calculation and a clamped-nuclei electronic calculation is reported.

		CP					
n_p		2	3				
ZnO		34 (25)	57 (48)				
α -SiO ₂		67 (56)	125 (114)				
		BP					
T_G		3	1	0.6	0.3		
ZnO		114 (67)	142 (95)	152 (105)	183 (136)		
α -SiO ₂		165 (110)	176 (121)	182 (127)	196 (141)		

tation of the nuclear relaxation term takes much longer than the clamped-nuclei electronic term (a greater fraction of the total for CP than for BP); ii) For the CP strategy, passing from $n_p = 2$ to $n_p = 3$ in the construction of the Hessian matrix implies an increase of the computation time by roughly a factor of 2, as expected; for the BP strategy tightening T_G gradually increases the wall-clock time, up to a factor of 2.4 (ZnO) for the range of T_G considered; iii) Evaluation of the nuclear relaxation term is faster with the CP approach. Based on the least expensive computational settings in both cases, for example, we see that 25 min is required for the CP scheme versus 67 for the BP method in the case of ZnO; the corresponding times for α -quartz are 67 and 165 min, respectively; iv) the CP quasi-analytical strategy always takes considerably less time to compute the total tensor than the BP one (more so for ZnO than α -quartz).

4 Conclusions

We have developed a new quasi-analytical method for computation of the “proper” piezoelectric tensor of crystals including both clamped-nuclei electronic

and nuclear relaxation contributions. This method, which has been implemented in the CRYSTAL code, is based on extending a recently presented CPHF/KS procedure for obtaining dipole derivatives and also on numerical differentiation of analytical gradients to obtain the Hessian matrix. Our strategy is compared with the commonly used Berry phase approach in terms of accuracy, numerical stability and computational performance. Using PBE calculations on ZnO and α -quartz, the present quasi-analytical strategy is documented to be an optimal alternative to the numerical Berry phase approach. Moreover, a fully analytical procedure can be envisioned – it would require analytical determination of the Hessian.

Our present implementation does not take full advantage of symmetry as yet. However, work is currently in progress to overcome this limitation, which exploits features already present in the CRYSTAL code. The overall treatment presented here can be extended to other properties requiring higher-order derivatives with respect to electric fields, such as photo-elasticity and piezo-optics. We intend to carry out these further developments in the near future.

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