First-principles study of the electrooptic effect in ferroelectric oxides

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We first present a method to compute the electrooptic tensor from first principles, explicitly taking into account the electronic, ionic and piezoelectric contributions. We then study the non-linear optical behavior of three paradigmatic ferroelectric oxides. Our calculations reveal the dominant contribution of the soft mode to the electrooptic coefficients in LiNbO₃ and BaTiO₃ and its minor role in PbTiO₃. We identify the coupling between the electric field and the polar atomic displacements along the B-O chains as the origin of the large electrooptic response in perovskite ABO₃ compounds.

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The electrooptic (EO) effect describes the change of refractive index of a material in a static electric field and is exploited in various technological applications. Ferroelectric ABO₃ compounds exhibit unusually large EO coefficients and are therefore materials of choice for optical devices. Since the seventies, LiNbO₃ EO modulators have been widely used in fiber-optic transmission systems. More recently, the experimental characterization of optical non-linearities requires high-quality single crystals that are not always directly accessible nor easy to make. Input from accurate theoretical calculations allowing to predict the non-linear optical behavior of crystalline solids would therefore be particularly useful.

For many years, theoretical investigations of non-linear optical phenomena were restricted to semi-empirical approaches such as shell models or bond-charge models. In the last decade, significant theoretical advances have been reported concerning first-principles density functional theory (DFT) calculations of the behavior of periodic systems in an external electric field and opened the way to direct predictions of various optical phenomena. Particularly, attention has been paid to the calculation of non-linear optical (NLO) susceptibilities and Raman cross sections.

In this Letter, we go one step further and present a method to predict the linear EO coefficients of periodic solids within DFT. Our method is very general, and can be applied to paradigmatic ferroelectric oxides: LiNbO₃, BaTiO₃ and PbTiO₃. We find that first-principles calculations are fully predictive, and provide significant new insights into the microscopic origin of the EO effect. In particular, we highlight the predominant role of the soft mode in the EO coupling of LiNbO₃ and BaTiO₃, in contrast with its minor role in PbTiO₃.

At linear order, the dependence of the optical dielectric tensor \( \varepsilon_{ij} \) on the static (or low-frequency) electric field \( \varepsilon \), is described by the linear EO tensor \( r_{ij\gamma} \):

\[
\Delta (\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r_{ij\gamma} \varepsilon_{\gamma},
\]

Throughout this paper, we follow the convention of using Greek and Roman indexes (resp.) to label static and optical fields (resp.). We write all vector and tensor components in the system of cartesian coordinates defined by the principal axes of the crystal under zero field. We also refer to the atomic displacements \( \tau_{\kappa\alpha} \) \( \kappa \) labels an atom and \( \alpha \) a cartesian direction \) within the basis defined by the zone-center transverse optic (TO) phonon eigendisplacements \( u_{m}(\kappa\alpha) \):

\[
\tau_{\kappa\alpha} = \sum_{m} \tau_{m} u_{m}(\kappa\alpha).
\]

Let us first consider the clamped (zero strain) EO tensor, \( r_{ij\gamma}^{\eta} \), in which all electric-field induced macroscopic strains are forbidden. This is achieved experimentally by working at a frequency sufficiently high to avoid strain relaxations but low compared to the frequency of the TO modes. Within the Born-Oppenheimer approximation, we express the total derivative of \( \varepsilon_{ij} \) as the sum of two partial derivatives with respect to \( \varepsilon_{\gamma} \) and \( \tau_{m} \):

\[
\frac{d\varepsilon_{ij}}{d\varepsilon_{\gamma}} = \left. \frac{\partial\varepsilon_{ij}}{\partial\varepsilon_{\gamma}} \right|_{\tau=0} + \frac{4\pi}{\Omega} \sum_{m} \frac{\partial r_{ij\gamma}^{(1)}}{\partial\tau_{m}} \frac{\partial\tau_{m}}{\partial\varepsilon_{\gamma}}
\]

The derivative in the first term of the righthand side of Eq. (2) is computed at clamped atomic positions. It describes the electronic contribution to the EO tensor and is proportional to the NLO susceptibilities \( \chi_{ij\gamma}^{(2)} \). The second term represents the ionic contribution. It depends on the first-order change of the linear dielectric susceptibility due to atomic displacements, and is related to the Raman susceptibility \( \alpha_{ij}^{m}\kappa\alpha = \sqrt{\Omega} \sum_{\kappa\alpha} \frac{\partial r_{ij\gamma}^{(1)}}{\partial\tau_{m}} u_{m}(\kappa\alpha) \) of mode \( m \) \( \Omega \) is the unit cell volume, as well as to the amplitude of the ionic relaxation induced by the field \( \varepsilon_{\gamma} \). \( \partial\tau_{m}/\partial\varepsilon_{\gamma} \) can be expressed in terms of (i) the TO phonon mode frequencies \( \omega_{m} \) and (ii) the TO mode polarities \( p_{m\gamma} = \sum_{\kappa\beta} Z_{\kappa\gamma\beta}^{*} u_{m}(\kappa\beta) \), directly linked to the infrared (IR) intensities. Combining this with the previous equations, we obtain the clamped EO tensor.
\[ r_{ij\gamma}^n = -\frac{8\pi}{n_i^2 n_j^2} \chi_{ijl}^{(2)} \left| \right|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2} \sum_m \alpha_{ijm} \frac{p_m \gamma}{\omega_m^2} \] (3)

where \( n_i \) and \( n_j \) are the principal refractive indices.

Let us now consider the unclamped (zero stress) EO tensor, \( r_{ij\gamma}^n \). It can be shown \([14]\) that the macroscopic expression proposed in Ref. \([15]\) is still valid at the microscopic level so that the piezoelectric contribution to \( r_{ij\gamma}^n \) can be computed from the elasto-optic coefficients \( p_{ij\alpha\beta} \) and the piezoelectric strain coefficients \( d_{\gamma\alpha\beta} \)

\[ r_{ij\gamma}^n = r_{ij\gamma} + \sum_{\alpha,\beta=1}^{3} p_{ij\alpha\beta} d_{\gamma\alpha\beta}. \] (4)

An expression similar to Eq. (3) was previously used by Johnston \([16]\) to estimate the clamped EO tensor of LiNbO\(_3\) and LiTaO\(_3\) from IR and Raman measurements. However, this semi-empirical approach was limited by the indeterminacy of the relative sign of \( p_m \) and \( \alpha^{m} \). As discussed below, the direct evaluation of Eqs. (3) and (4) from first principles provides an easier and more accurate estimate of the EO tensor.

We have implemented this formalism in the ABINIT open source software \([17]\), within the local density approximation (LDA) to the DFT. The optical dielectric tensor, Born effective charges, phonon frequencies and eigendisplacements are computed from linear response \([13]\). The piezoelectric strain coefficients \( d_{\gamma\alpha\beta} \) are deduced from the piezoelectric stress coefficients \( e_{\gamma\alpha\beta} \) and the elastic constants. These two quantities, as well as the elasto-optic tensor \( p_{ij\alpha\beta} \), are obtained from finite differences.

The non-linear response functions \( \chi_{ijl} \) and \( \partial \chi_{ijl} / \partial \tau_{\alpha\alpha} \) are computed from a perturbative approach using a new implementation based on the \( 2n+1 \) theorem. To reach reasonable k-point sampling convergence, we combined the recently proposed PEAD expression \([3]\) and the finite difference formula of Marzari and Vanderbilt \([18]\) to compute the perturbation expansion of the polarization. More details will be provided elsewhere \([14]\). The method was tested on various cubic semiconductors and provides results in close agreement with earlier studies \([10, 11]\).

For BaTiO\(_3\) and PbTiO\(_3\), we use extended norm-conserving pseudopotentials \([19]\), a plane-wave kinetic energy cutoff of 45 hartree and a \( 10 \times 10 \times 10 \) k-point grid. For LiNbO\(_3\), we use the same norm-conserving pseudopotentials as in Ref. \([21]\) as well as the Born effective charges, phonon frequencies and eigenvectors already reported in that paper. For this compound, a \( 8 \times 8 \times 8 \) k-point grid and a plane-wave kinetic energy cutoff of 35 hartree give converged values for \( \chi_{ijl}^{(2)} \) and \( \partial \chi_{ijl}^{(1)} / \partial \tau_{\alpha\alpha} \).

First, we study LiNbO\(_3\). This compound has a trigonal symmetry with 10 atoms per unit cell. The theoretical lattice constants and atomic positions are reported in Ref. \([21]\). LiNbO\(_3\) undergoes a single transition at 1480 K from a centrosymmetric high-T paraelectric \( R3c \) phase to a ferroelectric low-T \( R3c \) ground state. The form of the EO tensor depends on the choice of the cartesian axes. Here, we follow the I.R.E. Piezoelectric Standards \([21]\).

With this choice of axes, the EO tensor in the ferroelectric phase of LiNbO\(_3\) has 4 independent elements (Voigt notations): \( r_{13}, r_{33}, r_{22} \) and \( r_{51} \). The TO modes can be classified into \( 4A_1 + 5A_2 + 9E \). The \( A_1 \) and \( E \) modes are Raman and IR active. Only the \( A_1 \) modes couple to \( r_{13} \) and \( r_{33} \), while the \( E \) modes are linked to \( r_{22} \) and \( r_{51} \).

In Table I, we also report the unclamped EO coefficients in LiNbO\(_3\). As the piezoelectric coefficients \( d_{31} \) (-1 pC/N) and \( d_{33} \) (6 pC/N) are small compared to \( d_{15} \) (55.9 pC/N) and \( d_{22} \) (21.6 pC/N), the piezoelectric effect is important for \( r_{31}^5 \) and \( r_{51}^1 \) and negligible for \( r_{13}^1 \) and \( r_{33}^1 \). The unclamped EO coefficient \( r_{31}^5 \) is nearly twice as large as the clamped one. Moreover, its theoretical value is in better agreement with the experiment than that of the clamped one. This suggests that the piezoelectric contribution was not entirely eliminated during the measurement of \( r_{31}^5 \); the correct value of the clamped coefficient might be closer to the theoretical 14.9 pm/V.

Second, we study PbTiO\(_3\) and BaTiO\(_3\). Both compounds are stable at room temperature in a ferroelec-
### Electronic and Piezoelectric Contributions to the EO Tensor

**TABLE I:** EO tensor (pm/V) in LiNbO$_3$; electronic, ionic and piezoelectric contributions, and comparison with experiment, for the clamped and unclamped cases. The ionic part is split into contributions from TO modes (ω$_m$ in cm$^{-1}$).

|       | A$_4$-modes | E-mode       |       | A$_4$-modes | E-mode       |       |
|-------|--------------|--------------|-------|--------------|--------------|-------|
|       | ω$_m$ r$_{13}$ r$_{33}$ | ω$_m$ r$_{22}$ r$_{33}$ |       | ω$_m$ r$_{13}$ r$_{33}$ | ω$_m$ r$_{22}$ r$_{33}$ |       |
| Electronic | 1.0 4.0 | 0.2 1.0 | Ionic | 243 6.2 18.5 | 155 3.0 7.5 | TO1 |
|       | 287 0.2 0.4 | 218 0.4 1.5 | TO2 |
|       | 355 0.1 0.0 | 264 0.6 1.3 | TO3 |
|       | 617 2.8 4.8 | 330 0.3 1.2 | TO4 |
|       | 372 -0.2 0.4 | 384 -0.1 0.2 | TO5 |
|       | 428 0.2 0.2 | 585 0.7 2.1 | TO6 |
|       | 677 0.0 0.0 |       | TO9 |
| Sum of ionic | 8.7 22.9 | 4.4 13.9 | Strain | 0.8 0.1 | 3.0 13.7 | Clamped |
| Present | 9.7 26.9 | 4.6 14.9 | Exp. | 8.6 30.8 | 3.4 28 | TO1 |
|           | 12 | 39 | 6 | 19 | TO2 |
| IR+R | 25.9 | 20.5 | Exp. | 10.5 | 27.0 | 7.5 | 28.6 |
| BCM | Exp. | 10.0 | 32.2 | 6.8 | 32.6 | Exp. | 9.9 |

### Raman Susceptibilities and Mode Polarities

**TABLE III:** Raman susceptibilities and mode polarities (10$^{-2}$ a. u.) of the A$_1$ TO modes in LiNbO$_3$, BaTiO$_3$ and PbTiO$_3$.

|       | LiNbO$_3$ | BaTiO$_3$ | PbTiO$_3$ |
|-------|-----------|------------|-----------|
|       | px | α$_{11}$ | α$_{33}$ | px | α$_{11}$ | α$_{33}$ | px | α$_{11}$ | α$_{33}$ |
| TO1 | 3.56 | -0.70 | -2.02 | 1.22 | -0.16 | -1.13 | 1.25 | -0.57 | -0.43 |
| TO2 | 0.45 | 0.30 | 0.53 | 3.25 | -1.18 | -2.73 | 2.18 | -0.75 | -0.33 |
| TO3 | 0.67 | 0.18 | 0.05 | 1.74 | -1.26 | -2.55 | 2.68 | -2.42 | -2.28 |

In the latter two compounds, the magnitude of r$_{33}^n$ is dominated by one particular phonon mode. In BaTiO$_3$, the TO2 mode at 300 cm$^{-1}$ has a similar strong overlap (92%) with the unstable mode in the paraelectric phase than the TO1 modes in LiNbO$_3$, as previously discussed. In PbTiO$_3$, all A$_1$ modes contribute almost equally to r$_{33}^n$. The TO2 mode at 357 cm$^{-1}$ has the strongest overlap (73%) with the soft mode in the cubic phase. Surprisingly, its contribution to r$_{33}^n$ is 23.5 times smaller than the contribution of the TO2 mode in BaTiO$_3$.

To identify the origin of the distinctive behavior of PbTiO$_3$, we report in Table III the mode polarities and Raman susceptibilities of the A$_1$ TO modes. In the three compounds, α has two independent elements α$_{11}$ and α$_{33}$ that determine the amplitude of r$_{13}^n$ and r$_{33}^n$. α$_{33}$ is large for the TO1 mode in LiNbO$_3$ and the TO2 mode in BaTiO$_3$. On the other hand, it is the smallest for the TO2 mode in PbTiO$_3$, in agreement with experiments. Combined with a higher frequency (ω$_{p_{35}}$/ω$_{p_{35}}$ = 1.41), a lower polarity (p$_{35}$/p$_{35}$ = 1.49), and a larger value of the refractive index (n$_{p_{35}}$/n$_{p_{35}}$ = 1.35), this weak Raman susceptibility (α$_{p_{35}}$/α$_{p_{35}}$ = 8.27) explains the weak contribution of the TO2 mode to r$_{33}^n$ in PbTiO$_3$.
Changing the mass of Pb to that of Ba in the dynamical matrix of PbTiO$_3$ has no significant effect on the relative Ti–O displacement. Large atomic displacements of opposite direction along the Ti–O chains are therefore needed to generate a large $\alpha_{33}$ and potentially a large $r_{33}$.

In summary, we presented a method to compute the EO tensor from first principles. In LiNbO$_3$ and BaTiO$_3$, the large EO response originates in the giant contribution of the successor of the soft mode, which combines low frequency, high polarity and high Raman susceptibility. In comparison, the contribution of the similar mode in tetragonal PbTiO$_3$ is rather weak due to its low Raman susceptibility. In the perovskites, the Raman susceptibility is principally determined by the atomic displacements along the B–O chains in the polar direction. This suggests that the search for new perovskite oxides with good EO properties should focus on compounds with large relative B–O atomic displacements along the chains.

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## TABLE IV: Decomposition of the Raman susceptibility of the A$_1$ TO2 mode in BaTiO$_3$ and PbTiO$_3$ into contributions from the individual atoms in the unit cell (23).

|       | BaTiO$_3$ | PbTiO$_3$ |
|-------|-----------|-----------|
| $\kappa$ | $\sqrt{\frac{\Delta \chi_{\alpha \beta}^{(1)}}{\delta r_{\alpha \beta}^2}} u(\kappa, 3) \alpha_{33}(\kappa)$ | $\sqrt{\frac{\Delta \chi_{\alpha \beta}^{(1)}}{\delta r_{\alpha \beta}^2}} u(\kappa, 3) \alpha_{33}(\kappa)$ |
|       | (a.u.) | (a.u.) |
| Ba/Pb | 0.45 | -0.014 | -0.01 | -40.00 | 0.01 |
| Ti    | -6.46 | 0.257 | -1.66 | -2.64 | 0.216 | -0.57 |
| O$_1$ | 5.15 | -0.167 | -0.86 | 3.69 | 0.059 | 0.22 |
| O$_2$/O$_3$ | 0.43 | -0.240 | -0.10 | -0.02 | -0.316 | 0.01 |
| Tot   | -2.73 | -0.32 |