Dielectric properties and Raman spectra of ZnO from a first principles finite-differences/finite-fields approach

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Using first principles calculations based on density functional theory and a coupled finite-fields/finite-differences approach, we study the dielectric properties, phonon dispersions and Raman spectra of ZnO, a material whose internal polarization fields require special treatment to correctly reproduce the ground state electronic structure and the coupling with external fields. Our results are in excellent agreement with existing experimental measurements and provide an essential reference for the characterization of crystallinity, composition, piezo- and thermo-electricity of the plethora of ZnO-derived nanostructured materials used in optoelectronics and sensor devices.

ZnO is a wide-band gap, transparent, polar semiconductor with unparalleled optoelectronic, piezoelectric, thermal and transport properties, which make it the material of choice for a wide range of applications such as blue/UV optoelectronics, energy conversion, transparent electronics, spintronic, plasmonic and sensor devices. Understanding the infra-red (IR) properties of the bulk crystal is crucial for the intrinsic characterization of the material and is a prerequisite for the viable application of all ZnO-derived systems (e.g. nanostructures, interfaces, alloys) that are now the leading edge of research in many optoelectronic fields. In fact, at IR wavelengths, the vibrational polar modes affect also the dielectric response of the material (i.e. the optical properties), and thus its final performance. This justifies the uninterrupted sequence of experimental reports on vibrational properties of wurtzite ZnO crystal, which started in the sixties and continues nowadays.

Raman spectroscopy is one of the most common investigation techniques exploited for this purpose because it provides information on the structural and chemical properties such as orientation, crystallinity and existence of defects and impurities. However, despite the profuse research efforts pursued in the last decades, there are still open questions on the unambiguous identification of high-frequency phonon modes or unusual line-width variations and the interpretation of angular-dependent Raman spectra of ZnO: The uniaxial crystal structure along with the pronounced mass difference and the strong bond polarity imparts a large LO-TO splitting that mixes phonon bands and makes the interaction with external radiation largely anisotropic. Clearly, a unified theoretical approach able to treat at the same level of accuracy both the phonon dispersion and the Raman spectra is highly desirable. Although semiempirical approaches could provide a simple and computationally inexpensive way to treat this problem, the parameterization of the force fields strongly reduces the transferability of the interatomic potentials, which must be carefully tested for each specific system and morphology especially in the presence of doping, defects and impurities. On the other hand, while a few attempts to reproduce ZnO phonon bands through ab initio techniques exist, no simulations of Raman spectra have appeared so far. The challenge resides in the proper treatment of the response of a highly polar material like ZnO to external electric fields.

In principle, Density Functional Perturbation Theory (DFPT) is an elegant and accurate approach for simulation of both phonon and Raman spectra. In practice, the required computational effort, and the difficulty in improving the description of the electronic structure beyond the common functional approximations (LDA, PBE, etc.) prevent the application of this techniques for a large class of realistic structures and materials. ZnO is a prototypical example: a standard Density Functional Theory (DFT) description of the band structure of bulk ZnO severely underestimates the band gap ($\Delta E_{\text{DFT}}^{\text{gap}} = 0.9$ eV vs $\Delta E_{\text{exp}}^{\text{gap}} = 3.3$ eV). This is not simply due to the lack of many-body corrections typical of DFT, but rather to an unphysical enhancement of the covalent character of the Zn-O bonds. In turn, the wrong description of the electronic structure affects the electrostatic properties of the system and thus the phonon distribution and the coupling with the external fields. This problem...
may be easily overcome by including Hubbard-like corrections\textsuperscript{16} or using hybrid functionals\textsuperscript{17}. However, these features are not readily accessible in DFPT approaches for their large computational cost\textsuperscript{16}.

In this paper we have solved the problem of simulating with comparable accuracy both the electronic and vibrational spectrum of ZnO using a unified finite-fields/finite-differences approach that is independent of the choice of the functional. This allows us to simulate the phonons, the high and low-frequency dielectric constant and the nonresonant Raman spectra of any material through a finite set of electronic structure and force calculations using the finite displacement method\textsuperscript{19}.

\section*{Results}

\subsection*{Unified finite-fields/finite-differences theory}

The interatomic Force Constants (IFCs) $K$ and the electronic susceptibility $\gamma$ are obtained as finite differences of forces and polarizations with respect to atomic displacements or external electric fields\textsuperscript{20}.

IFCs are the second derivatives at equilibrium of the total energy versus the displacements of the ions $u(R)$, or alternatively, the derivative of the atomic forces $F$ versus the ionic displacements:

$$K_{ij,kl}(\mathbf{R} - \mathbf{R}) = \left. \frac{\partial^2 E_{\text{tot}}}{\partial u_{ij}(\mathbf{R}) \partial u_{kl}(\mathbf{R})} \right|_{\mathbf{R}},$$

where $R$ and $R'$ are Bravais lattice vectors, $I$, $J$ are the $I$-th and $J$-th atom of the unit cell, and $x$ and $y$ represent the Cartesian components. Phonon frequencies ($\omega_{ij}$) and normal modes ($u_{ij}^n$) are routinely obtained from the resolution of the eigenvalue equation:

$$\sum_{kl} \mathbf{D}_{ij,kl} \mathbf{u}_{kl} = \omega_{ij} \mathbf{u}_{ij},$$

where the dynamical matrix $D_{ij,kl}$ is the Fourier transform of the IFC. The acoustic sum rule (ASR) in real space is defined as in Ref. 12, while long-wavelength dipole-dipole effects are included by means of specific non-analytical correction to the IFCs, as proposed by Yi Wang et al.\textsuperscript{13}.

The proper treatment of the long wavelength macroscopic polarization field requires also the evaluation of the dielectric tensor and of the Born effective charges. For this purpose we consider the electronic susceptibility:

$$\chi_{ij} = \frac{\varepsilon_s}{\varepsilon_0} \frac{\partial^2 E_{\text{tot}}}{\partial E_{ij}},$$

where $E_{\text{tot}}$ is the total energy in the presence of electric field $E_{ij}$ and $P_s^l$ is the electronic polarization along the direction of $E$. Here, $E_{\text{tot}}$ and $P_s^l$ are evaluated following the method proposed by Umari and Pasquarello\textsuperscript{20}, where the introduction of a non local energy functional $E_{\text{tot}}[\psi] = E[\psi] + E_{\text{corr}}(\text{PM} + \text{PD}[\psi])$ allows electronic structure calculations for periodic systems under finite homogeneous electric fields. $E_s$ is the ground state total energy in the absence of external electric fields; $P^S$ is the usual ionic polarization, and $P^l$ is given as a Berry phase of the manifold of the occupied bands\textsuperscript{20}.

The high-frequency dielectric tensor $\varepsilon^\infty$ is then computed as $\varepsilon_{ij}^\infty = \delta_{ij} + 4\pi \chi_{ij}$ and the Born effective charge tensor $Z_{ij}$ is defined as the induced polarization along the direction $j$ by a unitary displacement of the $I$-th atom in the $i$ direction, or alternatively in terms of atomic forces in the presence of the electric field $E$:

$$Z_{ij} = \Omega \frac{\partial P_j^l}{\partial E_{ij}} = \frac{\partial^2 E_{\text{tot}}}{\partial E_{ij} \partial E_{ij}} = \frac{\partial E_{\text{tot}}}{\partial E_{ij}}.$$

Finally, the contribution of the polar optical modes to the static dielectric constant $\varepsilon^0 = \lim_{\omega \to 0} \varepsilon(\omega)$ is computed using the Lyddane-Sachs-Teller relation\textsuperscript{11,13}:

$$\varepsilon_{ij}^0 = \alpha_{ij}^0 (\omega_L) / \alpha_{ij}^0 (\omega_T)$$

where $\omega_L$ (LO) and $\omega_T$ (TO) are the LO (TO) phonon frequencies and $s$ denotes the electric field polarizations parallel $(||)$ and perpendicular $(\perp)$ to the polar axis. This alternative method is implemented and fully integrated in the QUANTUM ESPRESSO suite of codes (www.quantum-espresso.org; the finite-fields/finite-differences approach is implemented in the package FD in PHonon.).

The calculation of the Raman spectra proceeds along similar lines. The non-resonant Raman intensity for a Stokes process is described by the Placzek’s expression\textsuperscript{24}:

$$I \propto \sum_m |e_i \cdot x^m |^2 |e_j |^2 (n_m + 1) / \omega_m,$$

where $e_i$ and $e_j$ are the polarization of the incident (scattered) radiation, $\omega_m$ is the frequency of the generated optical phonon, $n_m$ is the Bose-Einstein distribution, and $x^m_{ij}$ is the Raman tensor, defined as:

$$x^m_{ij} = \sqrt{\Omega} \sum_{kl} x_{ijkl}^m u^m_{kl}.$$

Within the finite-field approach, the third rank tensor $x^m_{ijkl}$ is evaluated in terms of finite differences of atomic forces in the presence of two electric fields\textsuperscript{25}:

$$x^m_{ijkl} = \frac{\partial x_{ij}}{\partial \varepsilon_{kl}} = \frac{\partial^2 P_s^l}{\partial \varepsilon_{kl} \partial \varepsilon_{ij}} = \frac{1}{\Omega} \frac{\partial^2 E_{\text{tot}}}{\partial \varepsilon_{kl} \partial \varepsilon_{ij}}.$$

In practice, the tensor $x^m_{ijkl}$ is obtained from a set 19 calculations, which combine the finite electric fields $\varepsilon_{ij}$ along the coordinate direction, $x^m_{ijkl}$ is then symmetrized to recover the full $C_{6h}$ symmetry of the wurzite structure.

\section*{Dielectric and vibrational properties}

The calculated high and low frequency dielectric constants, summarized in Table I, are in agreement with experimental spectroscopic ellipsometry data\textsuperscript{21}, as well as Hartree-Fock calculations\textsuperscript{26}. Born effective charges (Table I) are also in agreement with values extracted from transverse IR reflectance spectra\textsuperscript{27}, and may be easily associated to piezoelectric properties of ZnO and its modifications under pressure\textsuperscript{26}.

PBE and PBE + U phonon dispersions are reported in Fig. 1 and phonon frequencies at the Brillouin Zone center ($\Gamma$) are summarized in Table II, where we also display the LDA values for comparison. Experimental Inelastic Neutron Scattering (red diamond and blue circles) and Raman (green squares) data are extracted from Ref. 7 and superimposed in Fig. 1 to the first principles data. While LDA and PBE results clearly underestimate the experimental frequencies, mostly in the optical branches, with PBE + U the agreement is very good. Here only the highest-frequency LO bands are slightly overestimated. Notably, these phonon branches suffer of anharmonic renormalization effects, which are not included in the present approach. Furthermore, the error bar on the experimental Raman results is higher for these bands, due to the low cross-section of the corresponding phonon-photon scattering processes (see below).

Following the irreducible representation of the wurzite symmetry group $C_{6h}$, the phonon modes of ZnO can be classified as $\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2$. One low energy $A_1$ and one double $E_1$ modes correspond to the transverse and longitudinal acoustic branches, the others are optical modes. $B_1$ modes are IR and Raman inactive. The two $E_2$ modes are non polar IR inactive but Raman active. In $A_1$

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$\omega$ & $\varepsilon^\infty$ & $\varepsilon^0$ & $Z^*$ \\
\hline
$\omega_L$ & 3.14 (3.78) & 7.76 (8.91) & 2.12 \\
$\omega_T$ & 3.08 (3.70) & 6.98 (7.77) & 2.06 (2.02) \\
\hline
\end{tabular}
\caption{High-frequency ($\varepsilon^\infty$) and static ($\varepsilon^0$) dielectric constant and effective Born charges ($Z^*$) of wurzite ZnO, for electric field polarization parallel and perpendicular to the c-axis. Corresponding experimental values are reported in parenthesis.}
\end{table}
and $E_1$ polar modes, atoms move parallel and perpendicular to the c-axis respectively and are the ones responsible for the LO-TO splitting. The labeling in Fig. 1 and Table II is based on the direct analysis of the phonon eigenmodes and their underlying symmetry. Note that PBE calculations give an incorrect ordering of the $B_1$ and $A_1$(LO) modes that is instead correct in PBE + U (see Table II).

**Raman spectroscopy.** We calculated the Raman spectra for different propagation ($k$) and polarization ($e_i,e_s$) directions of the incoming and scattering light, as shown in Fig. 2. We simulated the Raman spectra for different rotation angles ($\theta$) of the polarization vectors in the planes parallel (a-plane) and perpendicular (c-plane) to the c-axis. Following the standard experimental setups, for c-plane spectra we considered only parallel polarization of the incoming and scattered light $|z(x)x\rangle|z(y)y\rangle$. We used the Porto notation: symbols inside the parentheses indicate the direction of $e_i$ and $e_s$, while symbols outside the parentheses indicate the directions of propagation of light ($k$). In the a-plane case, two different orientations of $e_i$, can be experimentally detected: $y(y)x\rangle|y(y)x\rangle$, and $y(x)x\rangle|y(x)x\rangle$.

Results for room temperature boson distribution are summarized in Fig. 2. Panel (a) shows the a-plane spectra for parallel polarization vector configurations, which reproduces the angular modification of experimental spectra$^{1,4}$ and the reciprocal intensity ratio of the main peaks. The spectra are, in fact, dominated by Stokes processes due to the $A_1$(TO) and $E_2$(low) phonon modes at 384 and 436 cm$^{-1}$, respectively, only 2 cm$^{-1}$ from the experimental values. The intensity of the $A_1$(TO) peak is independent from the orientation of incident polarization, while the $E_2$(low) peak reaches a maximum at 90° and minima at 0° and 180°. For 20°, 40°, 120°, and 140° a small contribution from $E_1$(TO) also appears at 410 cm$^{-1}$. The $E_1$(high) phonon mode at 106 cm$^{-1}$ is not visible in this energy scale, the LO modes are not allowed by symmetry for this incident light direction.

Similar arguments apply for the a-plane spectra for $e_i \perp e_s$ polarizations, as displayed in panel (b). Here the main contributions stem from the $E_1$(TO) and $E_1$(high) modes, whose reciprocal intensity depends on the $\theta$ angle. The two peaks are in counterphase: the former has maxima at 0°, 90°, and 180°, while the latter reaches the minimum, and vice versa. Besides these two peaks, experimental results for crossed polarization vectors exhibit small, angular-dependent features associated to $A_1$(TO) and $E_1$(LO) that should be symmetry forbidden in this geometry. This is indeed a consequence of the deviation from the ideal geometry set-up and/or a deviation from perfect hexagonal crystallinity of the sample. Following Ref. 8 we considered non-orthogonal polarization vectors, $e_i = \frac{1}{\sqrt{1+p^2}} \begin{pmatrix} \cos \theta \\ p \\ \sin \theta \end{pmatrix}$, $e_s = \frac{1}{\sqrt{1+p^2}} \begin{pmatrix} -\sin \theta \\ p \\ \cos \theta \end{pmatrix}$, through the inclusion of an arbitrary constant $p$. The angular distribution and intensity of the peaks depend on the choice of the $p$ factor, i.e. on the characteristic crystallinity of the sample. Results for $p = 0.5$ are reported in the inset of panel (b) where the $A_1$(TO) peak and a small contribution from $E_1$(LO) appear. From the spectra of Fig. 2 we can also extract the relative intensity ratio between the main Stokes peaks, which are univocally related to the non-zero matrix elements of the Raman tensor for the $C_{av}$ point group (see for instance Ref. 29). Calculated ratios between $A_1$ ($E_1$) and $E_1$(high), taken as reference, are 0.54 and 0.23, respectively, the corresponding experimental values are 0.6 and 0.4. The agreement is quite satisfactory for $A_1$, while it is slightly worse for $E_1$. However, in the latter case the experimental value is extracted from $e_i \perp e_s$ polarizations spectra, which may suffer of non-ideal hexagonal symmetry, as discussed above (Fig. 2b).

**Discussion**

Our results demonstrate that the coupled finite-fields/finite-differences DFT approach is essential to accurately evaluate the dielectric properties, phonon dispersions and Raman spectra of ZnO. By reducing high order derivatives of the total energy (i.e. of the charge density) to lower order differences of polarizations and forces obtained from a limited set of self-consistent DFT simulations, it favors the inclusion of advanced corrections to the ground-state electronic structure that are essential for the proper description of the system. In particular, the ground state electronic structure and the coupling with external fields in ZnO require the use of \textit{ad hoc} corrections to the position of the d-bands of Zn that can be achieved with a DFT + U treatment, as summarized in Fig. 3. In the case of
standard LDA and PBE calculations we observe a severe under-
overestimation of the bandgap (E_{gap}) and a wrong energy position of 
the d-bands of the Zn atoms, that in turn give an inadequate description 
of the phonon dispersions (see Fig. 1(b) and discussion therein). 
The choice of functional influences directly the electrostatics and 
thus also the characteristics of the vibrational response of the system. 
In fact, the IFCs are the sum of two contributions: 
\[ K^{\text{ion}}_{\alpha\beta}(R-R') = K^{\text{el}}_{\alpha\beta}(R-R') + K^{\text{ion}}_{\alpha\beta}(R-R') \] 
\hspace{1cm} (8) 
where \( K^{\text{ion}}_{\alpha\beta} \) are the second derivatives of Ewald sums 
corresponding to the ion-ion repulsion potential, while the electronic contributions \( K^{\text{el}}_{\alpha\beta} \) are the second derivatives of the electron-electron and 
electron-ion terms in the ground state energy. It is the last term that 
reflects directly in the vibrational spectrum the wrong position of the 
d-states and the dramatic underestimation of the gap. On the other 
hand, LDA, with its overestimation of the bonding (shorter lattice 
parameter and stiffer IFCs) accidentally gives results that are 
marginally closer to the experimental data thanks to a fortuitous cancel-
lation of errors. The inclusion of the Hubbard U, by correcting the 
d-Zn p-O hybridization, properly describes not only the electronic 
bands but also the vibrational and dielectric properties in agreement 
with the experimental results\(^{15}\). Notably, the values of the dielectric 
constants obtained with LDA (\( \epsilon_r = 5.37, \epsilon_{\perp} = 5.39 \)) and PBE 
(\( \epsilon_r = 5.24, \epsilon_{\perp} = 4.97 \)) are much higher than in experiments, a clear 
indication of a lesser polarity of the system in these approximations. 

Finally, the finite-fields/finite-differences framework allows 
straightforward developments of the theory to include 3rd order 
terms in the IFCs (i.e. anharmonic contribution to phonons) or 
susceptibility \( \chi^{(3)} \) for the simulation of non-linear optical properties 
such as hyper-Raman or electro-optic effects. One example of the 
latter is the Raman signal along the parallel c-plane \( z(xz)z(yz)z \) 
shown in Fig. 4, where the \( A_1(LO) \) and \( E_2^{(high)} \) modes dominate 
the spectrum for all angles (0–180°) (black solid line). However, 
although allowed by symmetry, \( A_1(LO) \) is invisible or hardly visible 
in most experimental data collections\(^{2,3,6,15} \). This effect is due to a 
competitive interaction with the Fröhlich term\(^3 \), which couples with 
the macroscopic field generated by the \( A_1(LO) \) mode and cancels 
most of the deformation potential contributions. This effect may be 
evaluated including a non-linear correction to the tensor \( \chi^{(1)}_{ijkl} \) for the 
longitudinal \( q_l \) mode\(^{10} \): 
\[ \frac{\partial \chi_{ij}}{\partial q_l} = \frac{\partial \chi_{ij}}{\partial q_l} |_{E=0} - \frac{8\pi}{\Omega} \sum_{\beta} \sum_{\alpha} \sum_{q_l} \chi_{ij}^{(2)} |_{q_l} \] 
\hspace{1cm} (9) 
where the third order tensor \( \chi_{ij}^{(2)} \) may be straightforwardly calculated 
extending the finite field approach to the case of three electric fields, 
or alternatively:
\[ \chi_{ij}^{(2)} = \frac{\partial^2 E_{\text{tot}}}{\partial E_{ij} \partial E_{\text{tot}}} = \frac{1}{4\pi} \frac{\partial \chi_{ij}^{(3)}}{\partial E_{\text{tot}}} \] 
\hspace{1cm} (10) 
Indeed, the inclusion of the Fröhlich term suppresses the \( A_1(LO) \) 
(red dashed line) in agreement with experiments.
In conclusion, we have demonstrated that our unified finite-fields/finite-differences technique provides a general framework for the calculation of the vibrational, dielectric and Raman properties of materials, without any limitation in the choice of the DFT framework. We have applied this method to the study of ZnO, a material that for its complex electronic structure requires a special treatment in order to obtain a faithful representation of its properties. Our results are in excellent agreement with available experimental data.

**Methods**

**Computational details.** We calculated vibrational and Raman spectra of wurtzite ZnO bulk using PBE+GGA\(^1\) ultrasoft pseudopotentials\(^2\), with a kinetic energy cutoff of 100 Ry. 3d electrons of Zn have been explicitly included in the valence for both cases. For PBE + U, a Hubbard-like potential with U = 12.0 eV and U = 6.5 eV is applied on the 3d orbitals of zinc and on the 2p orbitals of oxygen, respectively\(^3\). Note that the Hubbard U values included in the calculations do not have to be considered as physical on-site electron-electron screened potentials, in the sense of the many-body Hubbard Hamiltonian, but as empirical parameters introduced to correct the gap. This is an efficient and computationally inexpensive way to correct for the severe underestimate of the bandgap and the wrong energy position of the d-bands of the Zn atoms\(^4\). This procedure has also been applied to other similar systems\(^5\)–\(^8\).

For the calculation of phonon modes we considered a \((8 \times 8 \times 2)\) hexagonal supercell (512 atoms) and we calculated forces (i.e. IFC) displacing only 2 atoms in primitive ZnO cell along the two inequivalent directions. This corresponds to a set of 4 DFT calculations. The Raman tensor has been calculated on the primitive wurtzite cell.

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**Author contributions**
A.C. and M.B.N. designed the research, performed the calculations, analyzed the data and co-wrote the paper. M.B.N. wrote the finite-difference codes for phonon calculations. A.C. wrote the code for the finite-field calculation of the Raman tensor.

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