Polarization-based calculation of the dielectric tensor of polar crystals

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We present a novel method for the calculation of the static and electronic dielectric tensor of polar insulating crystals based on concepts from the modern theory of dielectric polarization. As an application, we present the first ab initio calculation of the dielectric constants in the wurtzite III-V nitrides AlN, GaN, and InN.

The modern quantum theory of polarization in dielectrics has been formulated only in recent years [1]. This development has opened a new era in the first principles theory of ferroelectricity and pyroelectricity [2]. The new theory has been used successfully to calculate, in a well defined and computationally efficient way, the macroscopic polarization changes induced by perturbations other than an electric field. Examples of such perturbations are e.g. lattice vibrations [3], ferroelectric distortions [2], and piezoelectric deformations [3,4], whereby the quantities being calculated are typically dynamical Born charges, spontaneous polarization, and piezoelectric constants.

So far, no direct attempt has been made towards the goal of determining the dielectric tensor (which of course quantifies the response to an external electric field) using polarization theory. In this Letter we present a novel method for calculating the static dielectric tensor of a crystal based on concepts from polarization theory; in particular, the method rests entirely on the evaluation of the dielectric polarization in zero field via the geometric quantum phase approach [1]. The method works in any polar material, i.e. any material having infrared-active zone-center modes. As an application, we provide the first (to our knowledge) determination of the dielectric constants.

The current method of choice for dielectric response calculations is Density Functional Perturbation Theory (DFPT) [3], a general and powerful approach to response properties. The method presented here, besides its different foundations, is less general but considerably simpler to implement than DFPT, and it may become a useful alternative.

The static dielectric tensor – The calculation of the dielectric tensor is highly non trivial, because it entails the determination of the electronic, as well as vibrational and elastic-piezoelectric, responses to an external electrostatic field. The elements of the dielectric tensor are

$$\varepsilon_{ij}^0 = \delta_{ij} + 4\pi \frac{dP_i}{dE_j},$$  \hfill (1)

where \( E \) is the screened macroscopic electrostatic field and \( P \) the macroscopic polarization resulting from the response of the electronic and ionic degrees of freedom. In the Born-Oppenheimer approximation the macroscopic polarization \( \mathbf{P} \) in the presence of a generic strain or electrostatic perturbation can be conveniently expressed as

$$\mathbf{P} = \mathbf{P}^0 + \mathbf{P}^{\text{lat}} + \mathbf{P}^E,$$

where the spontaneous component of the dielectric tensor, \( V \) is the bulk cell volume, \( \varepsilon_i \) the strain field, \( u_k^s \) the displacement of atom \( s \) from its equilibrium position; \( \varepsilon_{il}^{(0)} \) is the clamped-ion component of the piezoelectric tensor, and \( Z_{ik}^s \) the Born effective charge:

$$\varepsilon_{il}^{(0)} = \frac{\partial P^{\text{lat}}_i}{\partial \varepsilon_l}, \quad Z_{ik}^s = \frac{V}{e} \frac{\partial P^{\text{lat}}_i}{\partial u_k^s}. \hfill (4)$$

The spontaneous component of the polarization does not depend on strain and fields, and it is non-vanishing also in zero field. Using Eq. (4) and (5) we can rewrite Eq. (1) as

$$\varepsilon_{ij}^0 = \varepsilon_{ij}^\infty + 4\pi \sum_l \varepsilon_{il}^{(0)} \frac{\partial \varepsilon_l}{\partial E_j} \bigg|_u + \frac{4\pi e}{V} \sum_{sk} Z_{ik}^s \frac{\partial u_k}{\partial E_j} \bigg|_e \hfill (5)$$

We shall discuss first how the second and third term are evaluated, and then discuss the electronic dielectric tensor. The last two terms in Eq. (5) quantify the contributions of the macroscopic and microscopic structural

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degrees of freedom to the total polarization, respectively. In the absence of other total polarization, the strain field \( e_{il} \) and the atomic displacement \( u^s_{ij} \) are related to the screened field \( E \) by the condition of vanishing stress,
\[
\sigma_l = \sum_i e_{il} E_l - \sum_m \lambda_{lm} \epsilon_m = 0 \, ,
\]
and vanishing Hellmann-Feynman forces,
\[
F^s_l = \epsilon \sum_j Z^s_{ij} E_j + V \sum_{ls} \Xi^s_{il} \epsilon_l - \sum_{js} \Phi^s_{ij} u^s_{j} = 0 \, .
\]
The quantities appearing in Eqs. (6) and (7) are the elastic constants
\[
\lambda_{lm} = -\frac{\partial \sigma_l}{\partial \epsilon_m} - \sum_{is} \frac{\partial \sigma_l}{\partial u^s_{i}} \frac{du^s_{j}}{d \epsilon_m} \, ,
\]
the piezoelectric tensor
\[
e_{il} = \frac{\partial P_{il}}{\partial \epsilon_l} + \sum_{js} \frac{\partial P_{il}}{\partial u^s_{j}} \frac{du^s_{j}}{d \epsilon_l} = e^{(0)}_{il} + \sum_{jks'} Z^s_{ij} \Phi^{-1}_{jk} (\Xi^s)_{kl} \, ,
\]
and the harmonic force constants and internal strain parameters
\[
\Phi^s_{ij} = \left. \frac{\partial F^s_l}{\partial u^s_{ij}} \right|_\epsilon \, , \quad \Xi^s_{il} = \left. \frac{1}{V} \frac{\partial F^s_l}{\partial \epsilon_l} \right|_u \, .
\]
Combining Eq. (6) and (7), we obtain \( u \) and \( \epsilon \) as a function of the electric field:
\[
u^s_{i} = \sum_{jks'} \Phi^{-1}_{jk} (\Xi^s)_{kl} \left( e Z^s_{kjs'} + V \sum_{lm} \Xi^s_{il} \lambda_{lm} e_{mj} \right) E_j \, ; \quad (11)
\]
\[
\epsilon_i = \sum_{jk} \lambda^{-1}_{ik} e_{kj} E_j \, . \quad (12)
\]
These relations are the first two key ingredients of our method. Substituting them into Eq. (5), we obtain after some manipulation the following general expression for the static dielectric tensor:
\[
\epsilon^0_{ij} = 4 \pi e^2 \frac{1}{V} \sum_{kls} Z^{ss}_{ik} \Phi^{-1}_{kl} Z^{ss'}_{lj} + 4 \pi \sum_{mn} e_{im} \lambda^{-1}_{mn} e_{nj} + \epsilon^\infty_{ij}
\]
\[
= \epsilon^0 + \epsilon^b + \epsilon^\infty_{ij} \, .
\]
A central point of the above analysis is that all the ingredients of Eqs. (6) and (7) needed for Eq. (13) can be calculated from distorted and strained bulk cells using ab-initio total-energy and force calculations, supplemented by calculations of the dielectric polarization in zero field using the Berry-phase approach. The only exception is the electronic dielectric constant \( \epsilon^\infty \), for which an alternate approach has to be devised.

The electronic dielectric tensor – As we now show, \( \epsilon^\infty \) can be obtained using the relationship between macroscopic polarization in zero field and charge accumulation at the interfaces of an appropriately built homojunction of the material of interest. In an insulating superlattice consisting of periodically alternating slabs of equal length, stacked along direction \( \mathbf{n} \) and made of materials 1 and 2, the displacement field orthogonal to the interfaces is conserved: \( D_1 = E_1 + 4 \pi P_1 (E_1) = E_2 + 4 \pi P_2 (E_2) = D_2 \). (We use a scalar notation for the components of the vectors along \( \mathbf{n} \).) Expanding the polarization to first order in the screened fields in the two materials as \( P_1 (E) = P_i + \chi_i E_i \), with \( P_i \) the polarization in zero field and \( \chi_i \) the susceptibility, one obtains
\[
4 \pi (P_2 - P_1) = \epsilon^\infty_1 E_1 - \epsilon^\infty_2 E_2 \, .
\]
In the absence of zero-field (e.g. spontaneous) polarization, the familiar equality \( \epsilon^\infty_1 E_1 = \epsilon^\infty_2 E_2 \) is recovered. To proceed, we note that periodic boundary conditions imply \( E \equiv E_1 = -E_2 \), and \( \Delta E \equiv E_1 - E_2 = 2E \), so that
\[
4 \pi (P_2 - P_1) = \frac{1}{2} (\epsilon^\infty_1 + \epsilon^\infty_2) \Delta E \, .
\]
The charge accumulation per unit area at the interface between materials 1 and 2 is \( s_{\text{int}} \) and
\[
s_{\text{int}} = \pm 2 \mathbf{n} \cdot (P_2 - P_1) / (\epsilon^\infty_1 + \epsilon^\infty_2) \, , \quad (14)
\]
which connects the macroscopic bulk polarizations \( P_{1,2} \) at zero field with the components \( \epsilon^\infty_{1,2} \) of the dielectric tensors of the interfaced materials along the interface normal \( \mathbf{n} \).

In an undistorted homojunction, i.e. a superlattice in which material 1 is identical to material 2, there is no interface, no polarization change can occur, and the interface charge is zero. However, a polarization difference can be generated in a controlled manner by inducing a small distortion \( \delta \) of one of the atomic sublattices in half of the superlattice unit cell. The interface charge \( s_{\text{int}} \) accumulated at the interface between distorted and undistorted regions can be easily calculated via macroscopic averages. The zero field polarizations \( P_2 \) for the material in the undistorted state, and \( P_1 \) for the material in the same strain state as in the superlattice, are evaluated directly using the Berry phase technique. From Eq. (1), one
then extracts the average electronic dielectric constant
$$\varepsilon^\infty = (\varepsilon_1^\infty + \varepsilon_2^\infty)/2.$$  

In principle $\varepsilon_1$, the dielectric constant in the distorted
state, differs from the actual dielectric constant $\varepsilon_2$; thus,
so does $\varepsilon$. However, in the limit of zero distortion, $\varepsilon$
equals the component of the dielectric tensor along $\hat{n}$:
$$\varepsilon^\infty = \lim_{\delta \to 0} \varepsilon.$$  

This limit can be evaluated with essentially arbitrary accuracy by extrapolation or interpolation. The procedure
just outlined, yielding the electronic dielectric constants,
is the third key ingredient of the method.

In summary, in the present approach the static dielectric
constant is calculated via (i) calculation of the elastic
and force constants, (ii) calculation of the piezoelectric
tensor and Born charges, (iii) evaluation of the electronic
dielectric constants, (ii) calculation of the piezoelectric
and force constants, (ii) calculation of the piezoelectric
properties using their geometrical quantum phase; task (iii) also uses
relatively small, accurately controllable supercell calcu-
lations. In the latter, one must take care that (a) the slabs be short enough that the constant electric field will
not cause metallization, and that (b) the slabs be sufficiently
long to recover bulk-like behavior away from the interfaces.
Both requirements are generally met even by materials with small calculated gaps for sufficiently small
applied strains.

The quantities needed to evaluate the dielectric ten-
sor are usually obtained by means of DFPT [14]. The novelty of the present method is in the absence of a pertur-
bative approach, and in the determination of the elec-
tronic screening and piezoelectric properties using their
connection with the geometric quantum phase.

**Application to III-V nitrides** – We now apply the for-
malism just developed to the calculation of $\varepsilon^\infty_{33}$, the
component of the static dielectric tensor along the (0001)
axis at fixed lattice constant $c$, for the wurtzite III-V ni-
trides AlN, GaN, and InN [11]. Besides serving as a test of
the first ab initio theoretical prediction of the dielectric constant for these materials.

In the present case, only a few independent elements of the tensors described above are needed, namely those
containing derivatives of the total energy and polarization
with respect to the lattice constant $c$ and the in-
ternal structure parameter $u$. The piezoelectric constant
and the Born effective charge involved are
$$\varepsilon^\infty_{33} = c_0 \frac{\partial F_3}{\partial u} \bigg|_c + 2e Z^*_{33} \Phi_{33}^{-1} \Xi_{33}, \quad Z^*_{33} = \frac{\sqrt{3} a_0^2}{4e} \frac{\partial P_3}{\partial u} \bigg|_c.$$  

The force constant $\Phi_{33}$ (whence $\Phi_{33}^{-1} = 1/\Phi_{33}$ is ob-
tained) and the internal strain parameter $\Xi_{33}$ are calcu-
lated as derivatives of the Hellmann-Feynman force $F_3$
with respect to an atomic displacement from equilibrium,
and to a homogeneous strain of the lattice structure, re-
spectively:
$$\Phi_{33} = c_0^{-1} \frac{\partial F_3}{\partial u} \bigg|_c, \quad \Xi_{33} = \frac{4}{\sqrt{3} a_0^2} \frac{\partial F_3}{\partial c} \bigg|_u.$$  

The relevant inverse elastic constant is $\lambda_{33}^{-1} = 1/\lambda_{33}$, where
$$\lambda_{33} = c_0 \frac{\partial^2 \varepsilon_{33}}{\partial c^2} - V \Xi_{33} \Phi_{33}^{-1} \Xi_{33}.$$  

All calculations are done using density functional the-
ory in the local density approximation (LDA) to de-
scribe the exchange and correlation energy, and ultrasoft pseudopotentials [12] for the electron-ion interaction. A plane-wave basis cut off at 25 Ry and 12-point Chadi-
Cohen [13] mesh are found to give fully converged values
for the bulk properties. Given their known importance [14], the semicore $d$ states of Ga and In are included in the valence. The piezoelectric tensor and Born charges have been calculated [1] via the Berry phase technique [14]
using a 16-point Monkhorst-Pack [15] k-point mesh in the $a$-plane direction and 10 point uniform mesh in the $c$
direction, testing convergence up to 360 total points. For the $\varepsilon^\infty$ supercell calculation, we have employed (0001)-
oriented superlattices of typically 4 formula units (16 atoms), and typical cation sublattice displacements along
(0001) of 1-2 % of the bond length for AlN and GaN. Smaller displacements ($\sim 0.3$ %) were used for InN. 25
Ry cutoff and 12 k-points in the irreducible superlattice Brillouin zone guarantee convergence. No ionic relax-
ation is allowed, so that the response is purely electronic.

We report in Table I the calculated dielectric constants and their various components as given by Eq. (13) for
AlN, GaN, and InN, along with the available experimen-
tal data [16]. The electronic dielectric constants are very close to the experimental values for both AlN and
GaN, slightly larger for InN. The calculated static
constant agrees well with experiment for GaN, the only one
for which it is available experimentally. We also list the
values of the various constants contributing to $\varepsilon^\infty$ in Table I.

For AlN and GaN, the structural constants are simi-
lar, while the piezoelectric coefficient $\varepsilon_{33}$ is much higher
in AlN. InN behaves somewhat differently, as expected
from previous experience on other In compounds [16].

**Discussion** – In homopolar semiconductors, the ex-
ternal field does not cause distortions of the crystal lat-
tice, so that the static dielectric constant coincides with
the electronic one; our method as outlined above is not
applicable in this case, since no zero-field polarization
can exist in these materials. It does apply, however, to all
heteropolar materials, in which a polarization can always
be induced by appropriate atomic displacements. Apart
from the electronic response, a lower crystal symmetry
such as in wurtzites enables the action of screening me-
chanisms related to lattice distortions. As apparent from
of Eq. 13, the difference among $\epsilon^0$ and $\epsilon^\infty$ is due to the polarization induced by optically-active lattice vibrations (as quantified by the dynamical charges), and to the piezoelectric response, if any, along the appropriate axis (as measured by the piezoelectric constants). In a previous work 4 we have shown that AlN, GaN, and InN have large effective charges, and the highest piezoelectric coefficients amongst all tetrahedrally bonded semiconductors. Indeed (see Table I), the difference between static and high-frequency dielectric constants is large: in III-V nitrides the phonon-related term is comparable to the electronic one, and the piezoelectric component is about 10% of each of the other two. An important point to be noted is that the piezoelectric contribution cannot be neglected in an accurate calculation. This will be even more important in materials with large piezoelectric constants, such as ferroelectric perovskites.

In conclusion, we have presented a novel procedure for the calculation of the dielectric tensor based on the geometric quantum phase polarization theory. The method only uses bulk calculation, with the exception of a small supercell calculation, needed in the determination of the electronic dielectric constant. As an application, we have provided the first ab initio prediction of the dielectric constants of wurtzite AlN, GaN, and InN.

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[6] The polarization difference between any two states of a crystal, connected by an adiabatic transformation (labeled by $\lambda$) leaving the system insulating, is

$$\Delta P_e = - \frac{2e}{(2\pi)^3} \int_{\lambda_1}^{\lambda_2} d\lambda \int_{BZ} d\mathbf{k} \frac{\partial^2}{\partial \mathbf{k}^2} \phi^{(\lambda)}(\mathbf{k}, \mathbf{k}^\prime) \bigg|_{\mathbf{k}^\prime = \mathbf{k}} ,$$

where

$$\phi^{(\lambda)}(\mathbf{k}, \mathbf{k}^\prime) = \text{Im} \ln(\det S^{(\lambda)}(\mathbf{k}, \mathbf{k}^\prime))$$

is the geometric quantum Berry phase, and

$$S^{(\lambda)}_m(\mathbf{k}, \mathbf{k}^\prime) = \langle u_m^{(\lambda)}(\mathbf{k}) | u_m^{(\lambda)}(\mathbf{k}^\prime) \rangle$$

is the overlap matrix of lattice periodic wavefunctions $u^{(\lambda)}$ at different crystal momenta. Since the adiabatic transformation should leave the system insulating, the method does not allow a direct determination of $\epsilon^\infty$.
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| Material | $\epsilon^a$ | $\epsilon^b$ | $\epsilon^\infty_{33}$ | $\epsilon^0_{33}$ |
|----------|-------------|-------------|----------------|----------------|
| AlN | 5.06 | 0.64 | 4.61 | (4.68) |
| GaN | 4.44 | 0.15 | 5.69 | (5.70) |
| InN | 5.51 | 0.61 | 8.49 | (8.40) |

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|----------|-------------|-------------|----------------|----------------|
| AlN | 5.06 | 0.64 | 4.61 | (4.68) |
| GaN | 4.44 | 0.15 | 5.69 | (5.70) |
| InN | 5.51 | 0.61 | 8.49 | (8.40) |

*From Ref. [14], bRef. [17] and cRef. [18].
| ε_{33} | Z_{33}^* | Φ_{33} | Ξ_{33} | λ_{33} |
|--------|----------|-------|-------|-------|
|       | units C/m^2 | N/m | 10^9 N/m^3 | 10^11 N/m^3 |
| AlN   | +1.462   | -2.70 | +204 | +0.45 | +3.81 |
| GaN   | +0.727   | -2.72 | +209 | +0.38 | +3.80 |
| InN   | +1.092   | -3.02 | +155 | +0.32 | +2.22 |