Spontaneous polarization and piezoelectricity in boron nitride nanotubes

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Spontaneous polarization and piezoelectricity in boron nitride nanotubes show that they are excellent piezoelectric systems with response values larger than those of piezoelectric polymers. The intrinsic chiral symmetry of the nanotubes induces an exact cancellation of the total spontaneous polarization in ideal, isolated nanotubes of arbitrary indices. Breaking of this symmetry by inter-tube interaction or elastic deformations induces spontaneous polarization comparable to those of wurtzite semiconductors.

I. INTRODUCTION

Piezo- and pyroelectric materials for modern technological applications should display an excellent piezoelectric response, combined with high mechanical stability and low environmental impact. Existing materials, which can be broadly divided into the families of ceramics and polymers, can only partially fulfill the above requirements. Lead zirconate titanate (PZT) ceramics, for example, are strong piezo- and pyroelectrics but, unfortunately, they are also brittle, heavy and toxic. On the other hand, polymers like polyvinylidene fluoride (PVDF) are lightweight, flexible and virtually inert, but their polar properties are an order of magnitude weaker than those of PZT. In this paper, we examine spontaneous polarization and piezoelectricity in boron nitride nanotubes (BNNTs) in order to estimate their potential usefulness in various pyro- and piezoelectric device applications, and to understand the interplay between symmetry and polarization in nanotubular systems.

BNNTs, broadly investigated since their initial predictions and succeeding discovery are already well known for their excellent mechanical properties. However, unlike carbon nanotubes, most of BN structures are non-centrosymmetric and polar, which might suggest the existence of non-zero spontaneous polarization fields. Recently, these properties have been partially explored by Mele and Král, using a model electronic Hamiltonian. They predicted that BNNTs are piezo- and pyroelectric, with the direction of the spontaneous electric field that changes with the index of the tubes. The ab initio calculations presented in this paper provide a much fuller description and show that BNNT systems are indeed excellent lightweight piezoelectrics, with comparable or better piezoelectric response and superior mechanical properties than in piezoelectric polymers. However, contrary to the conclusions of Ref. 1 our combined Berry phase and Wannier function (WF) analysis demonstrates that electronic polarization in BNNTs does not change its direction but rather grows monotonically with the increasing diameter of the tube. Furthermore, the electronic and ionic spontaneous polarizations in BNNTs cancel exactly and these systems are pyroelectric only if their intrinsic helical symmetry is broken by, e.g., inter-tube interactions or elastic distortions.

The rest of this paper is organized as follows: Sec. II briefly reviews the formulation of the modern polarization theory in terms of Berry phases or Wannier functions. It also presents the details of the numerical techniques that were used to compute polarization. In Sec. III we discuss the results and the complementary nature of the two techniques to compute the spontaneous polarization. Finally, Sec. IV presents the summary and conclusions.

II. COMPUTATIONAL METHODS

A. Modern theory of polarization

The problem of computing polarization in materials is very subtle and is best approached by the “Berry-phase” method, introduced only a decade ago by Vanderbilt and King-Smith and Resta. Within this approach, the polarization difference between two states of a system is computed as a geometrical quantum phase. In practice, this difference, \( \Delta \mathbf{P} = \mathbf{P}(\lambda_1) - \mathbf{P}(\lambda_0) \), can be obtained if one can find an adiabatic transformation \( \lambda \) from one state to the other that leaves the system insulating. In the spirit of Ref. 10 \( \mathbf{P}(\lambda) \) can be split into two parts: \( \mathbf{P}_{\text{ion}}(\lambda) \) and \( \mathbf{P}_{\text{el}}(\lambda) \), corresponding to the ionic and electronic contributions respectively. In the case of paired electron spins, the expression for the total polarization of the system can be written as follows:

\[
\mathbf{P}(\lambda) = \mathbf{P}_{\text{ion}}(\lambda) + \mathbf{P}_{\text{el}}(\lambda) = \frac{e}{V} \sum_\tau Z_\tau r_\tau(\lambda) - \frac{2ie}{3\pi^2} \sum_{i,\text{occ}} \int_{BZ} dk \langle u_i^{(\lambda)} | \nabla_k | u_i^{(\lambda)} \rangle, \tag{1}
\]

where \( V \) is the volume of the unit cell, \( Z_\tau \) and \( r_\tau \) are the charge and position of the \( \tau \)-th atom in the cell, and \( u_i^{(\lambda)} \) are the occupied cell-periodic Bloch states of the system.
For the electronic part, an electronic phase $\varphi^{(\lambda)}_a$ (Berry phase) defined modulo $2\pi$ can be introduced as

$$\varphi^{(\lambda)}_a = V G_\alpha \cdot F^{(\lambda)}_e / e,$$

(2)

where $G_\alpha$ is the reciprocal lattice vector in the direction $\alpha$. Similarly, one can construct an angular variable for the ionic part, called in what follows the “ionic” phase, so that the total geometrical phase is

$$\Phi^{(\lambda)}_a = \sum_r Z_r^{(\lambda)} G_\alpha \cdot r_r^{(\lambda)} + \varphi^{(\lambda)}_a.$$

(3)

The total polarization in the direction $\alpha$ becomes

$$P^{(\lambda)}_a = e \Phi^{(\lambda)}_a / V;$$

(4)

where $R_\alpha$ is the real-space lattice vector corresponding to $G_\alpha$, $(R_\alpha \cdot G_\alpha) = 1$.

Alternatively, the electronic polarization of a system can be expressed in terms of the centers of charge of the Wannier functions of its occupied bands:

$$P^{(\lambda)}_{el} = -\frac{2e}{V} \sum_i \int \left| W^{(\lambda)}_i(r) \right|^2 dr = -\frac{2e}{V} \sum_i (r_i^{(\lambda)}),$$

(5)

where the Wannier function (WF) $W^{(\lambda)}_i(r)$ is constructed from the Bloch eigenstates $\psi^{(\lambda)}_{ik}$ of band $i$ using the unitary transformation

$$W_i(r) = \frac{V}{(2\pi)^3} \int_{BZ} e^{ikr} \psi_{ik}^{(\lambda)} dk,$$

(6)

and $(r_i^{(\lambda)})$ is the center of charge for the WF $W^{(\lambda)}_i$. However, because of the arbitrariness in the choice of the phases of the Bloch orbitals (non-uniqueness of transformation), there is no unique representation of the WFs of a given group of bands. In our approach, we employ an algorithm that has been recently developed by Marzari and Vanderbilt, which exploits the freedom in transformation to construct WFs that are as localized as possible. This is achieved by minimizing the sum of the quadratic spreads of the Wannier probability distributions $|W_j(r)|^2$,

$$\Omega = \sum_{j=1}^M [(r_j^2) - \langle r_j \rangle^2],$$

(7)

where the sum is over an isolated group of bands. The maximally localized WFs generated by this procedure are real, apart from an overall phase factor.

In both methods presented above, $P^{(\lambda)}_{el}$ can be obtained only modulo $2eR/V$ due to the arbitrariness in the choice of the phases of the Bloch functions. However, the difference in polarization $\Delta P$ is well defined if $|\Delta P_{el}| \ll |2eR/V|$. The same indetermination issues apply to $P^{(\lambda)}_{ion}$.

### B. Calculations

In computing the spontaneous polarization as the difference between a polar BNNT and a nonpolar reference state, a natural choice for the nonpolar state is a nanotube of the same geometry, but with boron and nitrogen atoms substituted by “pseudo carbon” atoms, which are 50% boron and 50% nitrogen. The adiabatic transformation is then defined by a “virtual crystal” procedure, in which parameter $\lambda$ corresponds to the content (in atomic %) of a site that is transformed from pure boron to the nonpolar reference state (vice-versa for nitrogen sites).

We used an ab initio multigrid-based total-energy method, employing a real-space grid as a basis for all the Berry phase calculations presented here. The Ceperley-Alder form, parametrized by Perdew and Zunger, was used for the exchange-correlation energy functional in the local density approximation. The norm-conserving pseudopotentials for all the elements, including virtual ones, were generated by the fhi19sp package utilizing the Kleinman-Bylander formulation.

To isolate the contribution of individual nanotubes, we performed polarization calculations for periodic crystals of noninteracting (i.e., positioned sufficiently far apart) nanotubes in hexagonal and tetragonal arrangements. The electronic structure calculations were carried out using two special $k$-points along the $Γ–A$ direction in the hexagonal or $Γ–Z$ direction in the tetragonal Brillouin zones. The $k$-space integration to compute $\varphi^{(\lambda)}_z$ was done on a string of 20 $k$-points uniformly distributed along the same direction and shifted to avoid the $Γ$-point. The internal consistency of our approach was checked against the results obtained using the ABINIT code for a few selected systems with excellent agreement.

Because of the different alignments of the polar bond with respect to the nanotube axis, we anticipate that the symmetry of the nanotube will play an important role in determining the magnitude of the spontaneous polarization field. In particular, since the zigzag geometry maximizes the axial dipole moment, we expect to observe the strongest effects in ($n, 0$) nanotubes.

### III. RESULTS AND DISCUSSION

#### A. Berry-phase method

The ionic part of the polarization in zigzag BNNTs, presented in Fig. 11, is large and directly proportional to the nanotube’s index. This is in contrast, for instance, to the corresponding wurtzite III-V and II-VI systems, where the spontaneous polarization can be viewed as the difference between the polarizations of the wurtzite (polar) and zincblende (nonpolar) geometries. Since these configurations become geometrically distinct only in the second shell of neighbors, their ionic phases are very close. The major contribution to the spontaneous polar-
ization in wurtzite materials is then due to the difference between the electronic polarizations (which are 0.04–0.08 C/m²), while in BNNTs both the ionic and the electronic contributions are essential.

The ionic phase differences ∆ϕ_{ion} between the polar and nonpolar configurations of zigzag nanotubes were evaluated via the virtual crystal approximation. In Ref. 7, the "family" has a zero ionic phase of the nonpolar reference configuration to set the phase of the nonpolar configuration to zero. Inset: ionic phase s discontinuities in ϕ_{ion}(λ) can be easily monitored, Berry phase calculations always produce phases that are smoothly folded into the [−π, π] interval and cannot be extrapolated. To obtain an unambiguous determination of the spontaneous polarization of BNNTs of arbitrary diameters, one has to compute the polarization in a different way, using the centers of charge of the WFs of the occupied bands (Eq. 5). Note that this approach does not solve the problem of branch indetermination, since while Berry phases are defined modulo 2π, Wannier centers are defined modulo a lattice vector \mathbf{R}. However, by shifting the indetermination from the phase to the lattice vector, we are able to map the electronic polarization problem onto a simple electrostatic model, where the unfolding of the electronic phase is straightforward.

This discrepancy is due to the ambiguity of the definition of electronic polarization as a multivalued quantity which can assume a lattice of values corresponding to Berry phases that differ by arbitrary multiples of 2π. Unlike the ionic phase model, where discontinuities in ϕ_{ion}(λ) can be easily monitored, Berry phase calculations always produce phases that are smoothly folded into the [−π, π] interval and cannot be extrapolated. To obtain an unambiguous determination of the spontaneous polarization of BNNTs of arbitrary diameters, one has to compute the polarization in a different way, using the centers of charge of the WFs of the occupied bands (Eq. 5). Note that this approach does not solve the problem of branch indetermination, since while Berry phases are defined modulo 2π, Wannier centers are defined modulo a lattice vector \mathbf{R}. However, by shifting the indetermination from the phase to the lattice vector, we are able to map the electronic polarization problem onto a simple electrostatic model, where the unfolding of the electronic phase is straightforward.

B. Maximally localized Wannier functions

The results of the maximally localized WF calculations for BNNTs are summarized in Fig. 2, where examples of the WFs for C and BN zigzag nanotubes of arbitrary diameter are shown, together with a schematic drawing that illustrates the shift of the Wannier centers in the adiabatic transformation from C to BN. Since

\[ P_{el}^{(BN)} = -\frac{2\epsilon}{V} \sum_i (\mathbf{r}_i^{(BN)} - \mathbf{r}_i^{(C)}), \]  

(8)

the magnitude of the shift of the centers is directly proportional to the electronic polarization of the BNNT with respect to the nonpolar CNT.

The σ-band WFs are centered in the middle of the C-C bonds in carbon nanotubes, while they are shifted

FIG. 1: Ionic-phase difference between the polar and nonpolar configurations for zigzag nanotubes; the ionic phase of the nonpolar configuration is set to zero. Inset: ionic phases wrapped into the [−π, π] interval. Phases are given in units of π.

FIG. 2: Electronic-phase differences between the polar and nonpolar configurations for zigzag nanotubes.
out that the Wannier function results are completely consistent with the Berry-phase calculations, since an electronic phase of $-n\pi/3$ for any $n$ can be folded, modulo $\pi$, into the three families found previously.

When we combine the results for the ionic and electronic phases into a general formula for the phase of an arbitrary $(n, m)$ BNNT,

$$\Delta \Phi_z^{\text{tot}}(n, m) = \Delta \phi_z^{\text{ion}}(n, m) + \Delta \phi_z^{\text{el}}(n, m)$$

$$= \frac{n - m}{3} - \frac{n - m}{3}, \quad (9)$$

we find that the two contributions cancel exactly and that the total spontaneous polarization in any BNNT is zero, i.e. the Wannier centers are arranged in such a way as to completely compensate the polarization due to ions. We have verified this result by two-point ($\lambda = 50$ and 100%) calculations of the Berry phase difference for a number of chiral nanotubes ((3,1), (3,2), (4,1), (4,2), (5,2) and (8,2)) and found an exact cancellation in all BNNTs, except for those narrower than approximately 4 Å, where a residual polarization is present as an effect of the very high curvature. In such nanotubes Wannier centers cannot fully compensate the ionic polarization, due to the severe distortion of the atomic bonds, which makes these systems weakly pyroelectric. For example, $P = 0.11$ C/m² in (3,1), 0.008 C/m² in (7,0) and 0.002 C/m² in (12,0) nanotubes.

The exact cancellation is a result of the overall chiral symmetry of the nanotubes which, although not centrosymmetric, are intrinsically nonpolar. Nevertheless, cancellation of ionic and electronic polarizations is exact only in the limit of an isolated BNNT. The spontaneous polarization in a nanotube bundle, where the chiral symmetry is effectively broken, is different from zero. For example, in (7,0) bundles at equilibrium distance of 3.2 Å $P \approx 0.01$ C/m². However, in this case it is hard to estimate the separate contributions to polarization due to bundling, extreme curvature and elastic deformation. Although smaller than in polymers or PZT, this polarization is comparable to some wurtzite pyroelectrics: e.g., $P = 0.06$ C/m² in $w$-ZnO.

\[ \text{C. Piezoelectricity} \]

The Berry-phase method can also be employed to compute piezoelectric properties of BNNTs, which are directly related to polarization differences between strained and unstrained tubes. In the linear regime, the change in polarization due to strain can be decomposed into a sum of two terms: a uniform axial strain and a relative displacement of the two sublattices. It is therefore natural to describe the geometry of a BNNT of a given radius in terms of an axial lattice constant $c$ and an internal parameter $u$, where $uc$ is the length of the vector connecting the anion with the cation. With this choice, the
The axial component of the Born dynamical charge tensor is

$$Z^* = (V/eNc_0)\partial P_3/\partial u$$

(13)

is the axial component of the Born dynamical charge tensor. Both polarization derivatives were computed as finite differences, changing $c$ or $u$ by $\pm 1\%$. The parameter $\xi = c_0 du/dc$, describing the change in the bond lengths under axial strain, was obtained by rescaling $c$ together with the associated components of ionic coordinates, and then relaxing the geometry of the system. For all the systems considered below, the value of $\xi$ is approximately the same and equal to -0.085.

We have calculated the piezoelectric properties for various bundles comprised of zigzag BNNTs with individual diameters ranging from 3.9 to 10.2 Å. These results are summarized in Table I and compared to a few well-known piezo- and pyroelectric materials. While the piezoelectric constants of zigzag BNNTs are modest when compared with inorganic compounds, they are still substantially larger than those in the PVDF polymer family.

### IV. SUMMARY AND CONCLUSIONS

In summary, we have investigated the spontaneous polarization and piezoelectric properties of BN nanotubes using state-of-the-art \textit{ab initio} methods. Our calculations demonstrate the complementary nature of Berry phase and Wannier function analysis, and show that a real-space description is necessary to unravel the Berry phases in complicated cases. The results suggest that BNNTs are excellent nonpolar piezoelectrics that exhibit substantially higher strain response than polar polymers. Moreover, we have shown that, contrary to the previous expectations, ideal non-interacting nanotubes are effectively nonpolar due to their intrinsic chiral symmetry, which leads to a total cancellation between the ionic and electronic polarizations. Breakage of this symmetry, as in the simple case of interacting nanotubes in a bundle, induces spontaneous polarization fields that are comparable to those of wurtzite semiconductors. Due to their piezo- and pyroelectric properties, BNNTs are excellent candidates for various nano-electro-mechanical applications.

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TABLE I: Piezoelectric properties of zigzag BNNT bundles.

| $(n, m)$ | diameter (Å) | $Z^*$ (e) | $|e_{33}|$ (C/m²) | Ref. |
|----------|--------------|------------|-----------------|------|
| (5, 0)   | 3.91         | 2.739      | 0.389           |      |
| (6, 0)   | 4.69         | 2.606      | 0.332           |      |
| (7, 0)   | 5.47         | 2.655      | 0.293           |      |
| (8, 0)   | 6.24         | 2.639      | 0.263           |      |
| (9, 0)   | 7.04         | 2.634      | 0.239           |      |
| (10, 0)  | 7.83         | 2.626      | 0.224           |      |
| (11, 0)  | 8.57         | 2.614      | 0.211           |      |
| (12, 0)  | 9.38         | 2.609      | 0.198           |      |
| (13, 0)  | 10.16        | 2.605      | 0.186           |      |

w-AIN    | 2.653        | 1.50       | [19]            |      |

w-ZnO    | 2.11         | 0.89       | [20]            |      |

PbTiO$_3$| 3.23         |           | [2]             |      |

P(VDF/TrFE) | ≈ 0.12       |           | [3]             |      |
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21 In the limiting case of flat C or BN sheets, the electronic polarization is zero for any value of λ, due to the existence of a threefold symmetry axis perpendicular to the surface of the sheet.
22 The data reported in Table III for nanotube bundles assume a close-packed geometry with intertube equilibrium distance of 3.2 Å.