

Electric Polarization of Heteropolar Nanotubes as a Geometric Phase

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The threefold symmetry of planar boron nitride (BN), the III-V analog to graphene, prohibits an electric polarization in its ground state, but this symmetry is broken when the sheet is wrapped to form a BN nanotube. We show that this leads to an electric polarization along the nanotube axis which is controlled by the quantum mechanical boundary conditions on its electronic states around the tube circumference. Thus the macroscopic dipole moment has an *intrinsically nonlocal quantum* mechanical origin from the wrapped dimension. We formulate this novel phenomenon using the Berry's phase approach and discuss its experimental consequences.

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Physical properties of materials at the nanoscale can differ dramatically from their bulk counterparts. This is especially evident in the electronic properties, since the quantum behavior of electrons on this scale is sensitive to the size, shape, and symmetry of the sample. Recent discovery of carbon nanotubes [1] provides a striking example, where metallic or semiconducting tubes of identical compositions have only slightly different radii [2–4]. Layered boron nitride (BN) provides a III-V analog to these materials; it can be formed in single and multiwall nanotubes that have the same Bravais lattice as their graphene counterparts, but with *inequivalent* atomic species on its two sublattices [5,6].

Here we show that the broken sublattice symmetry produces a macroscopic electric polarization in BN nanotubes, dependent on their topology. Remarkably, this ground state polarization is an *intrinsically nonlocal quantum* effect that cannot be described by a classical theory. The sign and size of the longitudinal polarization of the heteropolar tube are controlled by the boundary conditions on its electronic wave functions along its *wrapped* compact dimensions. We analyze this novel phenomenon by developing a quantum theory of the nanotube polarization in terms of a geometric phase [7–9].

A natural description of the electronic properties of this system is developed from an expansion of the tight binding Hamiltonian for the π electrons at small wave vectors q around the K and K' points at the corners of the Brillouin zone of the 2D hexagonal lattice [10,11]. Introducing the index $\alpha = \pm 1$ for these points then leads to the long wavelength Hamiltonians [10–12]

$$H_\alpha(q, \delta, \Delta) = \alpha \hbar v_F q \sigma_x + \delta_\alpha \sigma_y + \Delta \sigma_z, \quad (1)$$

where σ_μ are the 2×2 Pauli matrices, q is the wave vector along the tube axis, v_F is the Fermi velocity and Δ is a site diagonal potential that distinguishes the B and N sites. The crucial parameter $\delta_\alpha = \alpha \hbar v_F q_\perp$ is a contribution to the electronic gap that comes from the quantized crystal momentum q_\perp along its azimuthal direction.

We can interpret Eq. (1) as the Hamiltonian for an effective spin 1/2 particle interacting with a “magnetic field” defined by the parameters (q, δ, Δ) . H_α can be diagonalized by the rotation $U_\alpha(q, \delta, \Delta) = \exp(i\hat{\Omega}_\alpha \cdot \sigma/2)$, which aligns the vector

$$\hat{\Omega}_\alpha = (\alpha q, \delta_\alpha, \Delta) / \sqrt{q^2 + \delta_\alpha^2 + \Delta^2} \quad (2)$$

(units $\hbar v_F = 1$) in the z direction. The valence band eigenfunctions v_α of Eq. (1), relevant here, have energies $E_\alpha(q) = -\sqrt{q^2 + \delta_\alpha^2 + \Delta^2}$. They are obtained by the rotation of the down spinor $v_0 = (0, 1)$ according to $v_\alpha(q, \delta, \Delta) = \exp(i\hat{\Omega}_\alpha \cdot \sigma/2) \cdot v_0$, and correspond to the spin down state quantized along the local $\hat{\Omega}_\alpha$ axis.

The electric polarization of an extended system is ill defined as an intensive quantity, but its *changes* are well defined [8,9]. For an electronic Hamiltonian containing a control parameter $H(\lambda)$, the difference in polarization Δp between initial and final states at λ_i and λ_f can be obtained by integrating the differential changes in p as one adiabatically varies the control parameter λ

$$\Delta p = \int_{\lambda_i}^{\lambda_f} d\lambda \frac{\partial p}{\partial \lambda}. \quad (3)$$

We evaluate Δp on the path from the C nanotube, which is nonpolar by symmetry, to the heteropolar BN nanotube which can have a macroscopic dipole moment. We take as a control parameter the antisymmetric site diagonal potential Δ , where $\Delta_i = 0$ in the C nanotube. Therefore, integrating Eq. (3) over the range $0 < \Delta < \Delta_f$ gives an expression for the electric polarization of the heteropolar BN nanotube with the ionic strength Δ_f .

Equation (3) can be evaluated by studying the variation of $-i\langle v_\alpha | \partial / \partial q | v_\alpha \rangle$ as a function of Δ . Summing over α and wave vectors q , we find

$$\frac{p}{e} = \frac{1}{2\pi i} \sum_\alpha \int_0^{\Delta_f} d\Delta \int_{-\pi}^{\pi} dq \times \left(\left\langle \frac{\partial v_\alpha}{\partial \Delta} \middle| \frac{\partial v_\alpha}{\partial q} \right\rangle - \left\langle \frac{\partial v_\alpha}{\partial q} \middle| \frac{\partial v_\alpha}{\partial \Delta} \right\rangle \right). \quad (4)$$

The valence states v_α adiabatically follow the direction of the vector $-\hat{\Omega}_\alpha$, so that $\partial v_\alpha / \partial q = (-i/2)[\partial(\hat{\Omega} \cdot \sigma) / \partial q]v_\alpha$ and $\partial v_\alpha / \partial \Delta = (-i/2)[\partial(\hat{\Omega} \cdot \sigma) / \partial \Delta]v_\alpha$. Therefore, the polarization is

$$\frac{p}{e} = \frac{1}{4\pi} \sum_\alpha \int_0^{\Delta_f} d\Delta \int_{-\pi}^{\pi} dq \frac{\langle v_\alpha | \sigma_y | v_\alpha \rangle}{q^2 + \delta^2 + \Delta^2}. \quad (5)$$

Equation (5) has a simple geometric interpretation. The effective “spin” representation for each valence state v_α defines a unit vector field directed inward along the radial direction at each point (q, δ, Δ) in the parameter space for \mathcal{H}_α . The two surface integrals in (5) give the flux of

$$\int_0^{\Delta_f} d\Delta \int_{-\pi}^{\pi} dq \frac{\alpha \delta}{(q^2 + \delta^2 + \Delta^2)^{3/2}} = 2\alpha \arctan\left(\frac{W\Delta}{\delta\sqrt{\delta^2 + \Delta^2 + W^2}}\right). \quad (6)$$

It is intuitively clear that by interchanging the B and N sublattices, i.e., negating Δ , the sign of p should change. Much more profound is the fact that the dipole moment in Eq. (6) is also *odd* in δ , which thus reflects its essential quantum mechanical origin “rooted in the wrapped dimension.”

The macroscopic polarization is obtained by summing the allowed values of δ for each occupied subband in Eq. (6). When a BN sheet is wrapped into a tube, the transverse crystal momentum is quantized $q_{\perp,n}$, and this restricts the allowed values of δ in the sum. The transverse momenta $q_{\perp,n}$ depend on the subband index, n , and the wrapping vector $\vec{C}_{MN} = M\vec{T}_1 + N\vec{T}_2$ of the BN nanotube, where \vec{T}_1 and \vec{T}_2 are the primitive translation vectors for the hexagonal lattice [2–4,13]. A tube with wrapping indices (M, N) has a chiral index $\nu = \text{mod}(M - N, 3)$ [11] and its transverse momenta are quantized to the values $q_{\perp,n} = (2\pi/|\vec{C}_{MN}|)(n + \frac{1}{3}\text{sgn}\nu)$, so the gap parameter is $\delta_{\alpha n} = \alpha\hbar v_F q_{\perp,n}$. Thus summing Eq. (6) over subbands finally gives the net electric polarization

$$\frac{p}{e} = \frac{1}{2\pi} \sum_{\alpha n} \alpha \arctan\left(\frac{W\Delta}{\delta_{\alpha n}\sqrt{\delta_{\alpha n}^2 + \Delta^2 + W^2}}\right). \quad (7)$$

Note that the summand is *odd* in $\delta_{\alpha n}$, but *even* under the interchange $\alpha \leftrightarrow -\alpha$. Thus contributions to the electric polarization from states near the K and K' points are additive. However, a nonzero electric dipole moment occurs only when the momentum distribution around either point is odd in $\delta_{\alpha n}$. Thus the quantization of the transverse crystal momentum is the critical feature that controls the electric polarization of the BN nanotube.

Equation (7) predicts that BN nanotubes with crystal momentum distributions even in q_\perp are *unpolarized*. This happens in the limit of the flat BN sheet, for which the macroscopic dipole moment is obtained from an integral over all two-dimensional wave vectors, and for tubes with chiral indices $\nu = 0$, for which the kinematically allowed momenta occur in $\pm\delta_{\alpha n}$ pairs. A simple example of the latter occurs for the “armchair” $M = N$ structures with

a radial *inverse square* field in this parameter space that links through the two rectangular loops, shown in Fig. 1a. These are located at $\delta_{\alpha=\pm 1} = \pm\hbar v_F q_\perp$, oriented parallel to the $q - \Delta$ plane and extending from $-\pi < q < \pi$ and $0 < \Delta < \Delta_f$.

This flux is related by Stokes’ theorem to the line integral of an effective vector potential $\langle v_\alpha | \partial_{q(\Delta)} | v_\alpha \rangle$ around the loop perimeters, shown in Fig. 1b. Thus, the electric polarization is proportional to the solid angle that is “swept out” by the effective spin as it is adiabatically transported around the loops.

Introducing an energy cutoff at the bandwidth $W = \pi\hbar v_F$, the double integral in Eq. (5) gives

the mirror symmetry (or invariance under $M \leftrightarrow N$) [14]. Interestingly, Eq. (7) predicts a zero polarization even for “nonarmchair” tubes with $\nu = 0$.

However, for tubes with $\nu \neq 0$ the $\delta \leftrightarrow -\delta$ symmetry is broken by the *fractional quantization* of the transverse crystal momentum, and consequently these tubes have a net electric polarization with the sign determined by ν . This is a remarkable result, as it implies that two nearby structures (M, N) and $(M + 1, N)$ can have *opposing* electric dipole moments, even though their structures in the tangent plane of the tube are nearly identical.

A striking illustration of this effect is given in Fig. 2, in which we plot the electric polarization (the dipole moment per unit length in one dimension), calculated as a function of the symmetry breaking potential Δ , for three different “zigzag” tubes [14] with the nearby wrapping

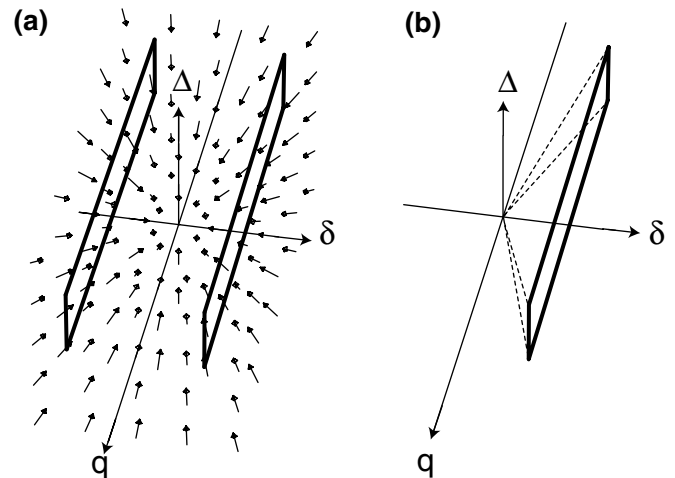


FIG. 1. (a) The electric polarization is the flux of a vector field linking through two rectangular loops in the space of Hamiltonian control parameters. (b) The flux through each rectangle is proportional to the solid angle subtended by the loop, which is also swept out by the vector $\hat{\Omega}$ when transported around the perimeter of the loop.

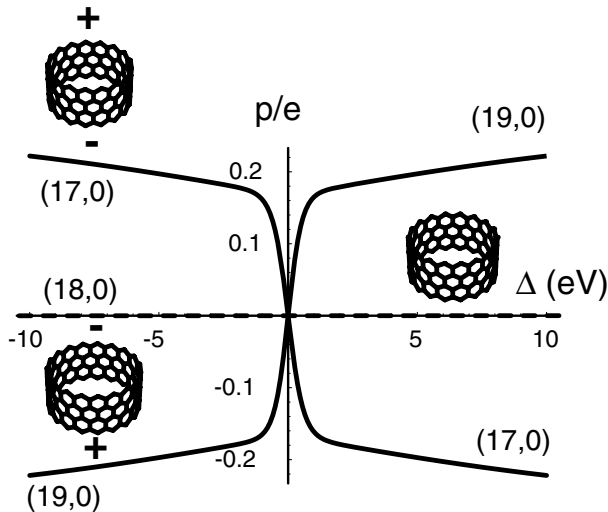


FIG. 2. The polarizations (dipole per unit length) for three heteropolar zigzag tubes are plotted as functions of their ionicity parameters Δ . The curves are labeled by the tube wrapping indices (M, N) , and the insets give their skeleton lattice structures. The $(18, 0)$ tube has no net polarization, while its neighbors $(18 \pm 1, 0)$ have nonzero electric polarizations of opposite sign.

indices $(M, N) = (17, 0)$, $(18, 0)$, and $(19, 0)$. Skeleton lattice structures for these three tubes are shown in the insets. We use the following parameters representative of BN: $\hbar v_F = 5.4 \text{ eV \AA}$, $W = 10 \text{ eV}$, and $\Delta = 2.5 \text{ eV}$, and plot the polarization in units of the elementary charge e .

Figure 2 shows that the electric polarization is *zero* for the $(18, 0)$ tube, and it is inverted for the $(17, 0)$ and $(19, 0)$ tubes, despite the fact that the three tubes have nearly identical local atomic structures in their surface planes. This reflects the interesting fact that the dipole moment arises as a *nonlocal* quantum effect that is controlled by the continuity of the electronic wave functions around the tube circumference and not any local property of the BN lattice. In this way, the circumferential boundary conditions for the electronic Bloch states can ultimately distinguish the three structures by their chiral indices ν .

The polarization (when nonvanishing) for BN tubes corresponds to a dipole moment of nearly $0.5D$ per unit cell. Its sign, determined by the chiral index ν , alternates with a three sublattice period as a function of the wrapping indices M and N . This effect is the heteropolar analog of three sublattice symmetry that distinguishes conducting and semiconducting behavior of graphene nanotubes [2–4]. Thus semiconducting graphene nanotubes with $\nu \neq 0$ may be classified into two families that are distinguished by the *sign* of their gap parameters. This controls the sign of the polarization induced by adiabatic introduction of the ionicity parameter Δ in Eq. (3).

The results derived here from the long wavelength Hamiltonian (1) give the contribution to the electric polarization from the π derived electronic states only. In general, one can expect additional contributions to

the electric dipole moment from lower lying σ bands. However, these contributions are not expected to show a strong dependence on the chiral index and are likely to be smaller in magnitude than the effects obtained here that are derived from the more polarizable π manifold. The periodic dependence of the electric polarization on the wrapping vector arises from the phase matching of the π -derived Bloch states around the tube circumference, and should be a fundamental property of any theory of electric polarization in these systems. Quantitative predictions for the electric polarization and piezoelectric couplings will require a microscopic theory that incorporates both the short wavelength physics (on the scale of the interatomic spacing) and the effects of the σ electrons.

Experimental observation of the macroscopic dipole moment of a heteropolar tube is complicated by the possibility that extrinsic or surface charges accumulated at the tube ends could mask the predicted intrinsic effects. Nevertheless, the polarization p in Eq. (7) defines (modulo e) the surface charge that must appear at the ends of the $\nu \neq 0$ heteropolar nanotube, *independent* of the atomic structure of the termination. Thus two-thirds of heteropolar single wall nanotubes should contain a universal but nonintegral surface charge, determined by the *bulk* electronic structure. Similarly junctions between inequivalent tube segments are predicted to localize interface charges $0, \pm p$, or $\pm 2p$ modulo e .

Multiwall heteropolar nanotubes would favor combinations which *compensate* the macroscopic dipole moment. For a double wall tube of outer radius a and inner radius b , one can estimate the electrostatic contribution to the surface energy

$$U_s = \frac{2z^2 e^2}{\pi|a-b|} K\left(-\frac{4ab}{(a-b)^2}\right), \quad (8)$$

where ze is the effective bound charge accumulated at the tube end and K is the complete elliptic integral of the first kind. Taking $z \approx 0.2$, $a \approx 10.4 \text{ \AA}$, and $b \approx 7.0 \text{ \AA}$ gives $U_s \approx 65 \text{ meV}$. Note that the structure of the double wall tubes grown under experimental conditions can be influenced by various kinetic factors as well.

Our model can be experimentally tested by measuring the *change* in polarization induced by varying control parameters in the Hamiltonian. Of particular interest is the effect of an elastic strain ϵ linearly coupled to the gap parameter $\delta \rightarrow \delta + \lambda\epsilon$. Thus the heteropolar tube is a *molecular piezoelectric* with the response constant $z^* = \partial p / \partial \epsilon = \lambda \partial p / \partial \delta$ given by

$$\frac{z^*}{e} = -\frac{\lambda}{2\pi} \frac{\Delta W(2\delta^2 + \Delta^2 + W^2)}{(\delta^2 + \Delta^2)(\delta^2 + W^2)\sqrt{\delta^2 + \Delta^2 + W^2}}. \quad (9)$$

The gap parameter δ can be linearly coupled to long wavelength compression, extension, or torsion of the tube depending on the wrapping indices [15]. These strains are

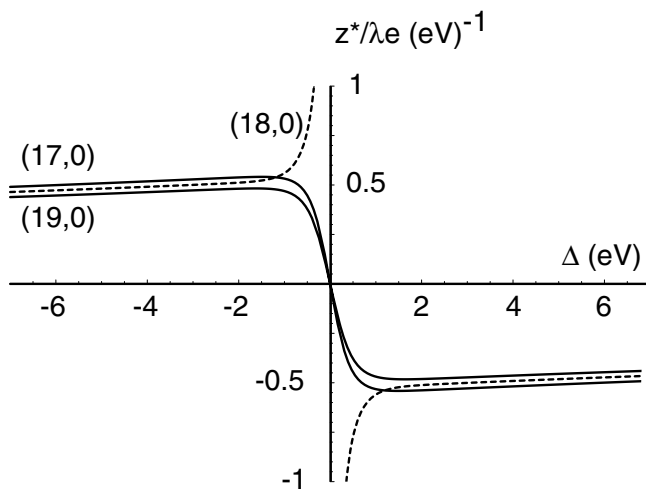


FIG. 3. The piezoelectric constants for the heteropolar zigzag (17,0), (18,0), and (19,0) tubes are plotted as a function of the ionicity parameter Δ .

the tube analogs to the orthorhombic and shear strains of an isolated graphene sheet.

In Fig. 3 we plot this piezoelectric constant as a function of the ionicity parameter Δ for the heteropolar (17,0), (18,0), and (19,0) nanotubes. Although the static dipole moments p/e for the (17,0) and (19,0) tubes have *opposite* signs, their piezoelectric constants z^*/e have the *same* signs. This is because the couplings of the gap to strain are nearly identical for the two structures. The piezoelectric constants should be large for the BN tubes, since we expect that $\lambda \approx 1$ eV, similar to carbon nanotubes. Note that the unstrained (18,0) tube has no static dipole moment but it has an exceptionally large piezoelectric constant that diverges proportional to $1/\Delta$ as $\Delta \rightarrow 0$. This occurs because $\Delta = 0$ marks a critical point, where the gap vanishes for tubes with chiral index $\nu = 0$. Figures 2 and 3 also demonstrate that BN realizes the “strongly ionic” limit of this problem, in which the static dipole and its piezoelectric coefficient are essentially saturated.

The electric dipole moments of heteropolar tubes provide crucial information for understanding their structures, elementary excitations, and phase behavior [16,17]. They are related, for example, with an assortment of new photogalvanic effects [11]. It is inevitable that other physical

phenomena and applications will derive from the unique properties of nanotubes with controllable electric polarization. This macroscopic phenomenon also provides a beautiful and experimentally relevant illustration of the important role of the geometric phase in quantum mechanics.

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