Electric Polarization of Heteropolar Nanotubes
as a Geometric Phase

E. J. Mele$^1$ and Petr Král$^2$

$^1$ Department of Physics, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
$^2$ Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

(Received )

The three-fold symmetry of planar boron nitride, 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.

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

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

(units $\hbar = 1$) in the $z$ direction. The valence band eigenfunctions $v_\alpha$ of Eqn. (1) are the solutions of $H_\alpha(q, \delta, \Delta) = \exp(i\hat{\Omega}_\alpha \cdot \sigma/2) \cdot v_0$, and correspond to the formation of the wavefunction $\alpha$ on the path from the C nanotube, which is nonpolar by symmetry, to the heteropolar BN nanotube with the ionic strength $\Delta$.

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

$$\Delta p = \int_{\lambda_i}^{\lambda_f} d\lambda \frac{\partial p}{\partial \lambda},$$

We evaluate $\Delta p$ 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 $\Delta$, where $\Delta_0 = 0$ in the C nanotube. Therefore, integrating Eqn. (3) over the range $0 < \Delta < \Delta_f$, gives an expression for the electric polarization of the heteropolar BN nanotube with the ionic strength $\Delta_f$.

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

$$p = \frac{1}{2e} \sum q \int_{0}^{\Delta_f} d\Delta \int_{-\pi}^{\pi} dq \left( \langle \frac{\partial v_\alpha}{\partial \Delta} \frac{\partial v_\alpha}{\partial q} \rangle - \langle \frac{\partial v_\alpha}{\partial q} \frac{\partial v_\alpha}{\partial \Delta} \rangle \right),$$

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 $[2–4]$. This is a consequence of the 2D electronic system forming in single and multiwall nanotubes that can be formed in single and multiwall nanotubes.

Layered BN provides a III-V analog to these materials; typical compositions have only slightly different radii $[2–4]$. The discovery of carbon nanotubes $[1]$ provides a striking example, where metallic or semiconducting tubes of identical compositions have only slightly different radii $[2–4]$. This is a consequence of the 2D electronic system forming in single and multiwall nanotubes that can be formed in single and multiwall nanotubes.

where metallic or semiconducting tubes of identical compositions have only slightly different radii $[2–4]$. The discovery of carbon nanotubes $[1]$ provides a striking example, where metallic or semiconducting tubes of identical compositions have only slightly different radii $[2–4]$. This is a consequence of the 2D electronic system forming in single and multiwall nanotubes that can be formed in single and multiwall nanotubes.

Where metallic or semiconducting tubes of identical compositions have only slightly different radii $[2–4]$. The discovery of carbon nanotubes $[1]$ provides a striking example, where metallic or semiconducting tubes of identical compositions have only slightly different radii $[2–4]$. This is a consequence of the 2D electronic system forming in single and multiwall nanotubes that can be formed in single and multiwall nanotubes.
The valence states $v_\alpha$ adiabatically follow the direction of the vector $-\hat{\Omega}$, 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

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

Equation (5) has a simple geometric interpretation. The effective “spin” representation for each valence state $v_\alpha$ defines a unit vector field directed inward along the radial direction at each point $(q, \delta, \Delta)$ in the parameter space for $H_\alpha$. The two surface integrals in (5) give the flux of a radial inverse square field in this parameter space that links through the two rectangular loops, shown in Fig. 1a. These are located at $\delta_\alpha = \pm \pm \hbar v_F q_\perp$, oriented parallel to the $q - \Delta$ plane and extending from $-\pi < q < \pi$ and $0 < \Delta < \Delta_f$.

![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 $\Omega$ when transported around the perimeter of the loop.](image)

This flux is related by Stokes’ theorem to the line integral of an effective vector potential $\langle v_\alpha | \partial_q | v_\alpha \rangle$ 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 Eqn. (5) gives

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

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

The macroscopic polarization is obtained by summing the allowed values of $\delta$ for each occupied subband in Eqn. (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 $\delta$ in the sum. The transverse momenta $q_{\perp,n}$ depend on the subband index, $n$ and the wrapping vector $C_{MN} = MT_1 + NT_2$ of the BN nanotube, where $T_1$ and $T_2$ are the primitive translation vectors for the hexagonal lattice [2–4]. A tube with wrapping indices $(M,N)$ has a chiral index $\nu = \text{mod}(M - N, 3)$ [14] and its transverse momenta are quantized to the values $q_{\perp,n} = (2\pi / |C_{MN}|)(n + \frac{1}{3} \text{sgn} \nu)$, so the gap parameter is $\delta_{\alpha n} = \alpha \hbar v_F q_{\perp,n}$. Thus summing Eqn. (6) over subbands finally gives the net electric polarization

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

Eqn. (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 wavevectors, 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 the mirror symmetry (or invariance under $M \leftrightarrow N$) [13]. Interestingly, Eqn. (6) 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 $\nu$. 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. 3, 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 $\Delta$, for three
different “zigzag” tubes with the nearby wrapping 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: \(h v_F = 5.4\text{eV Å} \), \(W = 10\text{eV}\) and \(\Delta = 2.5\text{eV}\), and plot the polarization in units of the elementary charge \(e\).

![Figure 2: The polarizations (dipole per unit length) for three heteropolar zigzag tubes are plotted as functions of their ionicity parameters \(\Delta\). The curves are labelled 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.](image)

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 wavefunctions 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 \(\nu\).

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 \(\nu\), 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. 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 \(\Delta\) in Eqn. 8.

The results derived here from the Hamiltonian [1] give the contribution to the electric polarization from the \(\pi\) derived electronic states. In general, one can expect additional contributions to the electric dipole moment from lower lying \(\sigma\) bands. However, these contributions are not expected to show a strong dependence on the chiral index and should be smaller than the effects derived from the more polarizable \(\pi\) manifold. Thus the periodic dependence of the electric polarization on the wrapping vector arises from the phase matching of the \(\pi\)-derived Bloch states around the tube circumference. It will be useful to quantify the relative \(\pi\)- and \(\sigma\)-derived contributions to the electric polarization within a complete microscopic theory.

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 Eqn. 7 defines (modulo \(\pi\)) 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 \(\pi\).

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

\[
U_s = \frac{2\pi^2e^2}{\pi(a - b)} K\left(-\frac{4ab}{(a - b)^2}\right),
\]

where \(ze\) is the effective bound charge accumulated at the tube end and \(K\) is the complete elliptic integral of the first kind. Taking \(z \approx 0.2, a \approx 10.4\text{Å}\) and \(b \approx 7.0\text{Å}\) 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 \(\epsilon\) linearly coupled to the gap parameter \(\delta \rightarrow \delta + \lambda\epsilon\). Thus the heteropolar tube is a molecular piezoelectric with the response constant \(z^2 = \partial p/\partial \epsilon = \lambda \partial p/\partial \delta\) given by

\[
\lambda = \frac{\pi(a - b)^2}{4ab}
\]
\[
\frac{z^*}{e} = -\frac{\lambda}{2\pi} \frac{\Delta W(2\delta^2 + \Delta^2 + W^2)}{(\delta^2 + \Delta^2)(\delta^2 + W^2)\sqrt{\delta^2 + \Delta^2 + W^2}}. \tag{9}
\]

The gap parameter \(\delta\) can be linearly coupled to long wavelength compression, extension or torsion of the tube depending on the wrapping indices \([13]\). These strains are the tube analogs to the orthorhombic and shear strains of an isolated graphene sheet.

![Graph](image_url)

**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 \(\Delta\).

In Fig. 3 we plot this piezoelectric constant as a function of the ionicity parameter \(\Delta\) 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 \(\Delta \to 0\). 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.

The work at the University of Pennsylvania was supported by the Department of Energy under Grants DE-FG02-01ER45118 and through the NSF through the Penn MRSEC under grant DMR 00-79909. We thank J. Bernholc and C.L. Kane for useful discussions. PK would like to acknowledge M. Shapiro for support.

[1] S. Iijima, Nature **354**, 56 (1991).
[2] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. **69**, 1579 (1992).
[3] J.W. Mintmire, B.I. Dunlap and C.T. White, Phys. Rev. Lett. **68**, 631 (1992).
[4] R. Saito, M. Fujita, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. Lett. **60**, 2204 (1992).
[5] N.G. Chopra et al. Science **269**, 966 (1995).
[6] X. Blase, A. Rubio, S.G. Louie and M.L. Cohen, Europhysics Lett. **28** 335 (1994).
[7] M.V. Berry, Proc. Royal Soc. London, Ser. A, **392**, 45 (1984).
[8] R.D. King-Smith and D.H. Vanderbilt, Phys. Rev. B **47**, 1651 (1993); *ibid*, Phys. Rev. B **48**, 4442 (1993).
[9] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
[10] C.L. Kane and E.J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).
[11] P. Král, E. J. Mele and D. Tománek, Phys. Rev. Lett. **85**, 1512 (2000).
[12] G.W. Semenoff, Phys. Rev. Lett. **53**, 2449 (1984).
[13] J.W. Mintmire and C.T. White, Phys. Rev. Lett. **81**, 2506 (1998).
[14] An armchair tube has one-third of the BN bonds oriented exactly along the azimuthal direction. The name is derived from the atomic motif repeated around the tube circumference which resembles an armchair. On a zigzag tube a chain of BN bonds “zigzags” around the tube circumference.
[15] L. Yang, N.P. Anantram, J. Han and J.P. Lu, Phys. Rev. B **60**, 13874 (1999).
[16] J.Gavillet, A. Louiseau, C. Journet, F. Willaime, F. Ducastelle and J.C. Charlier (preprint, 2001)
[17] B.G. Demczyk, J. Cumings, A. Zettl and O. Ritchie, Appl. Phys. Lett. **78**, 2772 (2001).