Comment on "Piezoelectricity in planar boron nitride via a geometric phase"

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Using the strain-dependent effective Hamiltonian and the geometric phase, Droth *et al.* [Phys. Rev. B **94**, 075404 (2016)] obtain an analytical expression for the electronic contribution to the piezoelectricity of planar hexagonal boron nitride (*h*-BN). Their analytical results of piezoelectric constants for *h*-BN are invalid because of the mistakes in constructing the adiabatic process of the piezoelectricity. In this Comment, we reconstruct a proper adiabatic process for piezoelectricity and formulate a general Berry phase expression for the piezoelectric coefficients of two-dimensional piezoelectric crystals by means of the modern theory of polarization. The corrected analytical results of the piezoelectric constants are in complete consistency with the first-principles calculations and hence manifest the validity and generality of the Berry phase expression of piezoelectric coefficients.

Recently, Droth *et al.* analytically evaluated the electronic contribution to the piezoelectricity of planar boron nitride (*h*-BN) by means of the geometric phase of wave functions and the strain-dependent effective Hamiltonian of *h*-BN [1]. The analytical value of piezoelectric constant e_{222} is 1.0×10^{-10} C/m, as shown in Eq. (14) of Ref. [1]. However, the value of e_{222} obtained from first-principles calculations is 3.71×10^{-10} C/m in the case of clamped-ion models [2]. Such large deviation of their analytical values from the first-principles calculations arises from a serious mistake in constructing the adiabatic process of the piezoelectricity. Consequently, the erroneous usage of the polarization difference formula in Eq. (4) leads to an invalid analytical expression of piezoelectric constant in Eq. (12) of Ref. [1]. In this Comment, we reconstruct a proper adiabatic process for piezoelectricity and present a general expression of the piezoelectric coefficients for two-dimensional (2D) piezoelectric crystals. For *h*-BN, the obtained analytical result agrees well with the first-principles calculations.

The modern theory of polarization offers further insight on the physical understanding of dielectricity, piezoelectricity, and ferroelectricity of crystalline systems [3–5], by virtue of the clear definition of the polarization difference, i.e., the accumulated bulk current through the crystals during the adiabatic evolving process from an initial state to a final state. In a quantum picture, the adiabatic current is essentially determined by the Berry phase of wave functions, i.e., the integral of the Berry curvature over the Brillouin zone [6]. Therefore, for the adiabatic evolving process parameterized by a scalar λ, from the initial state ($\lambda = 0$) to the final state ($\lambda = 1$), the polarization difference ΔP_i can be written

as [4–6]

$$\Delta P_i = 2e \sum_n \int_0^1 d\lambda \int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^2} \Omega_{i,\lambda}^n, \tag{1}$$

where factor 2 denotes the spin degrees of freedom and the Berry curvature of valence-band wave function u_n is defined by

$$\Omega_{i,\lambda}^n = i\left[\left\langle \frac{\partial u_n}{\partial k_i} \middle| \frac{\partial u_n}{\partial \lambda} \right\rangle - \left\langle \frac{\partial u_n}{\partial \lambda} \middle| \frac{\partial u_n}{\partial k_i} \right\rangle\right]. \tag{2}$$

Now let us first point out the mistakes made in Ref. [1] and then present the correct results. To explore the piezoelectricity of *h*-BN, Droth *et al.* construct an adiabatic process parameterized by the band gap δ and then choose free graphene as the initial state with $\delta = 0$ (zero band gap) and *h*-BN as the final state with $\delta = \Delta$ (where Δ is the band gap of *h*-BN). In this way, they write the polarization difference ΔP_i as [1]

$$\Delta P_i = 2e \sum_\tau \int_0^\Delta d\delta \int_{\text{BZ}/2} \frac{d\boldsymbol{q}}{(2\pi)^2} \Omega_{i,\delta}^\tau, \tag{3}$$

where τ denotes the K ($\tau = 1$) and K' ($\tau = -1$) valleys, and the corresponding Berry curvature is [1]

$$\Omega_{i,\delta}^\tau = i\left[\left\langle \frac{\partial u_\tau}{\partial q_i} \middle| \frac{\partial u_\tau}{\partial \delta} \right\rangle - \left\langle \frac{\partial u_\tau}{\partial \delta} \middle| \frac{\partial u_\tau}{\partial q_i} \right\rangle\right]. \tag{4}$$

Their chosen adiabatic process and parameter are incorrect for the piezoelectricity, because the correct adiabatic process of piezoelectricity should reflect the *deformation-induced polarization difference* from the initial state of undeformed *h*-BN to the final state of deformed *h*-BN. In fact, such an adiabatic process for the piezoelectricity of any 2D piezoelectric crystal can be captured by the λ-dependent strain

$$\boldsymbol{\varepsilon}(\lambda) = \lambda \Delta \boldsymbol{\varepsilon} = \lambda \begin{pmatrix} \Delta\varepsilon_{xx} & \Delta\varepsilon_{xy} \\ \Delta\varepsilon_{xy} & \Delta\varepsilon_{yy} \end{pmatrix}. \tag{5}$$

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Obviously, $\lambda = 0$ represents the initial state of the undeformed crystal, and $\lambda = 1$ denotes the final state of the deformed crystal. Consequently, the polarization difference along the i direction is contributed by all components of the strain tensor and takes the form

$$\Delta P_i = 2e \int_0^1 d\lambda \sum_{n,jk} \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^2} \Omega_{i,jk}^n \Delta \varepsilon_{jk}, \qquad (6)$$

where the Berry curvature $\Omega_{i,jk}^n$ of the valance band with respect to k_i and ε_{jk} is

$$\Omega_{i,jk}^n = i \left[\left\langle \frac{\partial u_n}{\partial k_i} \Big| \frac{\partial u_n}{\partial \varepsilon_{jk}} \right\rangle - \left\langle \frac{\partial u_n}{\partial \varepsilon_{jk}} \Big| \frac{\partial u_n}{\partial k_i} \right\rangle \right]. \qquad (7)$$

Equation (6) can be further simplified as

$$\Delta P_i = \sum_{jk} \left[\sum_n 2e \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^2} \Omega_{i,jk}^n \right] \Delta \varepsilon_{jk}. \qquad (8)$$

The piezoelectricity is generally defined as a reversible linear electromechanical coupling effect, and the flexoelectricity is an electromechanical response of stress and strain gradients [7]. Consequently, the piezoelectric coefficient, i.e., $e_{ijk} = (\partial P_i / \partial \varepsilon_{jk})|_{\varepsilon \to 0}$, can be written as

$$e_{ijk} = 2e \sum_n \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^2} \Omega_{i,jk}^n = \frac{e}{\pi} \sum_n C_{i,jk}^n, \qquad (9)$$

where $\Omega_{i,jk}^n$ is a short-hand notation of $\Omega_{k_i, \varepsilon_{jk}}^n|_{\varepsilon \to 0}$ (it will be used hereinafter) and $C_{i,jk}^n$ plays a similar role of the Chern number but is not quantized [6]. Equation (9) is a general Berry phase expression of the piezoelectric coefficient for any 2D piezoelectric crystal and can be further extended to the case of three-dimensional crystals.

Next, we reformulate the analytical expression of e_{222} for h-BN. Because the strain-induced pseudomagnetic vector potential keeps the time-reversal invariant, the valley degenerate remains. Therefore, we can only consider the low-energy effective Hamiltonian of h-BN at the K valley in the continuum approximation, as follows:

$$H_K(\mathbf{q}, \boldsymbol{\varepsilon}) = \Delta \sigma_z + \hbar v_F (\sigma_x q_x + \sigma_y q_y) + \hbar v_F (\sigma_x A_x + \sigma_y A_y), \qquad (10)$$

where $\hbar v_F = 3a|t|/2$, σ_x, σ_y and σ_z are the Pauli matrices, and the pseudomagnetic vector potential $\mathbf{A}$ as a perturbation in the Hamiltonian is given by [8]

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = -\frac{3t\beta}{4\hbar v_F} \begin{pmatrix} \varepsilon_{xx} - \varepsilon_{yy} \\ -\varepsilon_{xy} \end{pmatrix}, \qquad (11)$$

where $\varepsilon_{xx} = u_{xx}, \varepsilon_{yy} = u_{yy}, \varepsilon_{xy} = 2u_{xy}$, and $u_{ij} = (\partial_i u_j + \partial_j u_i)/2$, with the in-plane displacement $\mathbf{u}$. From the Hamiltonian in Eq. (10), we can obtain the energy eigenvalues and normalized eigenstates for the conduction (+) and valence (−) bands of h-BN without the strain perturbation, as follows:

$$E_\pm = \pm \sqrt{\hbar^2 v_F^2 (q_x^2 + q_y^2) + \Delta^2},$$

$$|u_\pm\rangle = \frac{1}{\sqrt{2E_+}} \begin{pmatrix} \frac{\hbar v_F (q_x - iq_y)}{\sqrt{E_+ \mp \Delta}} \\ \pm \sqrt{E_+ \mp \Delta} \end{pmatrix}. \qquad (12)$$

Using the identity

$$\langle \partial u_- / \partial R | u_+ \rangle = \langle u_- | \partial H_K(\mathbf{q}, \boldsymbol{\varepsilon}) / \partial R | u_+ \rangle / (E_- - E_+), \qquad (13)$$

with $R = q_i$ or ε_{jk}, one can rewrite the Berry curvature for the valence band of h-BN in Eq. (7) as

$$\Omega_{i,jk} = i \frac{\langle u_- | \partial H_K / \partial q_i | u_+ \rangle \langle u_+ | \partial H_K / \partial \varepsilon_{jk} | u_- \rangle - \text{c.c.}}{(E_+ - E_-)^2}, \qquad (14)$$

where c.c. denotes the complex conjugate. To obtain the Berry curvature $\Omega_{2,22}^K$ near the K point, we first write the partial derivatives of Hamiltonian in Eq. (10) with respect to q_y and ε_{yy} as

$$\partial H_K(\mathbf{q}, \boldsymbol{\varepsilon}) / \partial q_y = \hbar v_F \sigma_y, \quad \partial H_K(\mathbf{q}, \boldsymbol{\varepsilon}) / \partial \varepsilon_{yy} = \frac{3t\beta}{4} \sigma_x. \qquad (15)$$

Substituting Eqs. (12) and (15) into Eq. (14), we can obtain the Berry curvature $\Omega_{2,22}^K$ near the K point as follows:

$$\Omega_{2,22}^K = \frac{9at^2\beta\Delta}{16[(3at/2)^2(q_x^2 + q_y^2) + \Delta^2]^{3/2}}. \qquad (16)$$

Because the piezoelectric coefficient e_{222} of h-BN is mainly contributed by both of the Berry curvatures in the vicinity of K and K' points, the integral domain in Eq. (9) can be replaced by two circles centered at K and K' points, where the area of each circle should be equal to half of the first Brillouin zone in order to conserve the total number of states. Consequently, the piezoelectric coefficient e_{222} reads

$$e_{222} = \frac{4e}{(2\pi)^2} \int_0^{2\pi} d\theta \int_0^{q_m} \frac{9at^2\beta\Delta q dq}{16[(3at/2)^2 q^2 + \Delta^2]^{3/2}}, \qquad (17)$$

where the factor 4 contains both the spin and valley degenerates, $q = \sqrt{q_x^2 + q_y^2}$, and $\pi q_m^2 = S_{\text{BZ}}/2$ with the area of the first Brillouin zone $S_{\text{BZ}} = 8\pi^2/3\sqrt{3}a^2$. We simplify Eq. (17) and finally obtain the piezoelectric coefficient

$$e_{222} = \frac{e\beta}{2\pi a} \left(\frac{\Delta}{|\Delta|} - \frac{\Delta}{\sqrt{\sqrt{3}\pi t^2 + \Delta^2}} \right), \qquad (18)$$

where $\Delta/|\Delta| = 1$, because the band gap of the piezoelectric insulator h-BN is a positive constant with $\Delta = 3.0$ eV, as given in Ref. [1]. More generally, β is replaced by $\kappa\beta$ with the lattice correction factor κ, due to the lattice relaxation for the distorted h-BN. However, the clamped ion model requires that the original lattice remains, and hence $\kappa = 1$, for the clamped ion case. We adopt the same standard values of related parameters used in Ref. [1] for h-BN, i.e., $a = 1.44$ Å, $t = -2.3$ eV, $\Delta = 3.0$ eV, and $\beta = 3.3$. The calculated piezoelectric coefficient e_{222} is 2.99×10^{-10} C/m. If we further consider that the π-band electrons only contribute to 80% of the piezoelectricity for h-BN [9], we will obtain the piezoelectric coefficient e_{222} with its value 3.74×10^{-10} C/m, which agrees well with the result ($e_{222} = 3.71 \times 10^{-10}$ C/m) obtained from the first-principles calculations [2]. The agreement is a result of the correct piezoelectric polarization difference expression in Eq. (8) and the correct values of related parameters of h-BN rather than a numerical coincidence. One can also use the tight-binding piezoelectric approach to check the piezoelectric coefficient e_{222} with the same parameter values of h-BN [11]. Usually, the piezoelectric coefficient e_{ijk} is defined by

$e_{ijk} = \partial P_i / \partial \varepsilon_{jk}$ in Voigt notation, where ε_{jk} is the strain tensor component with $\varepsilon_{xx} = u_{xx}$, $\varepsilon_{yy} = u_{yy}$, and $\varepsilon_{xy} = 2u_{xy}$ for 2D systems. For this definition of piezoelectric coefficient, the $\bar{6}m2$ point group in hexagonal crystal system requires

$$e_{211} = -e_{222} = e_{112} = e_{121}. \tag{19}$$

However, if the piezoelectric coefficient e_{ijk} is written as $e_{ijk} = \partial P_i / \partial u_{jk}$ in Ref. [1], where $u_{jk} = (\partial_j u_k + \partial_k u_j)/2$, with $\boldsymbol{u}$ as the in-plane displacement, Eq. (19) needs to be rewritten as

$$e_{211} = -e_{222} = \tfrac{1}{2}e_{112} = \tfrac{1}{2}e_{121}. \tag{20}$$

We note that recent analytical results of the piezoelectric coefficients for h-BN and transition metal dichalcogenide monolayers are also obtained [10,11]. It should be emphasized that Eq. (18) in our Comment is only for the piezoelectric insulator h-BN. In Eq. (18), Δ is required to be nonzero by the definition of Berry curvature in Eq. (14). Normally, the physical intuition tells us that the piezoelectric coefficient is discontinuous for the transition from the semimetal graphene with both zero band gap and piezoelectricity to a piezoelectric insulator with both nonzero band gap and certain piezoelectric value. If e_{222} is expressed as a continuous function of the band gap Δ, that predicted piezoelectricity is really contrary to the physical intuition.

In conclusion, we formulate a general expression for the piezoelectric coefficients of 2D piezoelectric crystals by means of the Berry phase approach. Using the effective Hamiltonian in the continuum approximation, we analytically derive the expression for the piezoelectric constants of h-BN. The analytical result is in complete consistency with the first-principles calculations.

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