Surface polarization and edge charges

Yuanjun Zhou, Karin Rabe, and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA
(Dated: May 4, 2015)

The term “surface polarization” is introduced to describe the in-plane polarization existing at the surface of an insulating crystal when the in-plane surface inversion symmetry is broken. Here, the surface polarization is formulated in terms of a Berry phase, with the hybrid Wannier representation providing a natural basis for study of this effect. Tight binding models are used to demonstrate how the surface polarization reveals itself via the accumulation of charges at the corners/edges for a two dimensional rectangular lattice and for GaAs.

PACS numbers: 77.22.Ej, 73.20.-r, 71.15.-m

For over two decades, it has been understood that the electric polarization \( \mathbf{P} \) of an insulating crystal is a bulk quantity whose electronic contribution is determined modulo \( 2\pi \mathbf{R}/\Omega \) (where \( \mathbf{R} \) is a lattice vector and \( \Omega \) is the unit cell volume) by the Bloch functions through a Berry-phase expression, or alternatively, in real space through the charge centers of the Wannier functions \([1, 2]\). It was also shown that the macroscopic surface charge of an insulating crystal is predicted by the standard bound-charge expression \( \sigma_{\text{surf}} = \mathbf{P} \cdot \hat{n} \) (where \( \hat{n} \) is the surface normal) \([3]\), as illustrated schematically in Fig. 1(a).

Here, we introduce and analyze a related quantity, the “surface polarization,” defined as a 2-vector \( \mathbf{P} \) lying in the plane of an insulating surface of an insulating crystal. By analogy with the bulk 3-vector \( \mathbf{P} \), it has the property that when two facets meet, the linear bound-charge density appearing on the shared edge is predicted to be

\[
\lambda_{\text{edge}} = \mathbf{P}_1 \cdot \hat{n}_1 + \mathbf{P}_2 \cdot \hat{n}_2
\]

where \( \mathbf{P}_j \) is the surface polarization on facet \( j \) and \( \hat{n}_j \) is a unit vector lying in the plane of the facet and pointing toward (and normal to) the edge, as illustrated in Fig. 1(b).

This surface polarization \( \mathbf{P} \) is quite distinct from the dipole per unit area normal to the surface, which has also been called “surface polarization” by other authors \([1, 5]\). The latter is always present regardless of the symmetry of the surface, and manifests itself macroscopically through the surface work function. In contrast, our surface polarization \( \mathbf{P} \) lies in-plane and is nonzero only when the symmetry of the terminating surface supports a nonzero in-plane vector, as for example on the (110) surface of GaAs. It can also arise from a spontaneous symmetry-breaking surface reconstruction, as observed recently at the \( \text{Pb}_1-x\text{Sn}_x\text{Se} \) (110) surface \([6]\) and predicted for an ultrathin film of \( \text{SrCrO}_3 \) on \( \text{SrTiO}_3 \) substrate (001) \([7]\). The surface polarization will be most evident when the bulk \( \mathbf{P} \) vanishes, as will be the case for the systems discussed below.

The purpose of this Letter is to extend the Berry-phase theory to the case of surface polarization \( \mathbf{P} \) as defined above. To do this, we introduce a formulation based on hybrid Wannier functions (HWFs), which are Bloch-like parallel to the surface and Wannier-like in the surface-normal direction \([8, 11]\). This allows for the use of Berry-phase methods parallel to the surface while allowing a real-space identification of the surface-specific contribution in the normal direction. We illustrate the concept first for a “toy” 2D tightbinding (TB) model, demonstrating the method of calculating the surface polarization. We then consider an atomistic 3D model of an ideal (110) surface of a generic III-V zincblende semiconductor, using a TB model of GaAs to describe the electronic structure. In both cases, we confirm that the surface polarization correctly predicts corner and edge charges.

We first show how to express the surface polarization in terms of the Berry phases of HWFs for a 2D insulating sample, which we take to lie in the \((x, z)\) plane. We take the “surface” (here really an edge) to be normal to \( \hat{z} \) and introduce HWFs \( |h_{lj}(k_x)\rangle \), where \( l \) indexes unit-cell layers normal to the \( z \) direction and \( j \) runs over occupied Wannier functions in a single unit cell. For the bulk, the lattice is periodic in \( z \) as well as \( x \), and the \( |h_{lj}(k_x)\rangle \) and their centers \( \psi_{lj}^{\text{bulk}}(k_x) \) can be obtained using the 1D construction procedure given in Ref. [12]. To study the surface behavior we consider a ribbon consisting of a finite number of unit cells along \( \hat{z} \). We then construct and diagonalize the matrix \( Z_{mn} = \langle \psi_m(k_x)|z|\psi_n(k_x)\rangle \), whose eigenvectors yield the HWFs and whose eigenvalues give
the HWF centers \(z_{ij}(k_x)\). In practice these are easily identified with the bulk \(z_{ij}^{\text{bulk}}(k_x)\) covering the range of \(l\) values that define the ribbon, with only modest shifts induced by the presence of the surface, allowing a common labeling scheme for both.

If we were interested in computing the dipole moment normal to the surface, we could obtain this from an analysis of the \(k_x\)-averaged \(z\) positions \(z_{ij}\) of the HWFs, where \(a\) is the lattice constant along \(x\). However, our purpose here is different: we want to compute the polarization parallel to the surface. For this, we compute the Berry phase

\[
\gamma_{x,ij} = \int dk_x \langle h_{ij} | \frac{d}{dk_x} | h_{ij} \rangle.
\]

of each HWF “band” \((ij)\) as \(k_x\) runs across the 1D BZ. Doing the same for the bulk HWFs (these are independent of \(l\) and taking the difference, we obtain a set of Berry-phase shifts \(\Delta \gamma_{x,ij} = \gamma_{x,ij} - \gamma_{x,ij}^{\text{bulk}}\) from which the electronic surface polarization can be determined via

\[
P^{\text{elec}}_x = -\frac{e\alpha}{\Omega \pi} \sum_{ij=\text{top surf}} \Delta \gamma_{x,ij}
\]

where a factor of two has been included for spin degeneracy and \(\Omega\) is the edge repeat length \(a\) in 2D. Since \(\Delta \gamma_{x,ij}\) decays exponentially into the bulk, the sum will converge within a few layers of the surface, but for definiteness we sum to the center of the ribbon. If the \(z_{ij}\) values of some neighboring HWF bands overlap, the procedure needs to be generalized by grouping the HWFs into layers and using a multiband generalization to assign contributions to each layer.

The generalization to a 3D crystal with surface normal to \(z\) is straightforward. The HWFs are \(|h_{ij}(k_x, k_y)\rangle\) with centers \(z_{ij}(k_x, k_y)\). The surface polarization \(P_x^{\text{elec}}\) is then obtained by computing Berry phases with respect to \(k_x\) as before, averaging over all \(k_y\), and multiplying by the lattice constant \(a\) divided by the surface cell area \(\Omega\). The other surface polarization \(P_y\) is given by the same formalism but with \(x\) and \(y\) reversed.

In the models considered in this paper, the surface polarization is purely electronic, as the ions are held fixed in their bulk positions. More generally, \(P_x = P^{\text{ion}}_x + P^{\text{elec}}_x\) with the ionic contribution given by \(P^{\text{ion}}_x = \Omega^{-1} \sum_{\tau \ell} Z_\tau (X_{\ell \tau} - X^{\text{bulk}}_{\ell \tau})\), where \(Z_\tau\) and \(X_{\ell \tau}\) are the \(x\) position and bare charge of ion \(\tau\) in cell \(l\), and \(X^{\text{bulk}}_{\ell \tau}\) is the corresponding bulk position of the same atom.

To illustrate these ideas, we start by considering a tight-binding (TB) model of the simple 2D crystal shown in Fig. 2(a). We assume a rectangular lattice with an aspect ratio \(b/a \approx 0.8\). There are two atoms symmetrically located along a diagonal of the rectangular unit cell with coordinates \((\frac{1}{4}, \frac{1}{2})\) and \((\frac{3}{4}, \frac{3}{2})\), so that the bulk crystal has inversion symmetry. We consider only one \(s\) orbital per atom with onsite energy taken to be zero, and assume that each atom contributes one electron so that only the lower band is (doubly) occupied. We take the nonzero hoppings to be those shown in Fig. 2(a) and choose their values to be \(t_1 = -2.2\), \(t_2 = -0.15\), and \(t_3 = -0.1\), \(t_4 = -0.09\) and \(t_5 = -0.06\) in eV. The position operators are taken to be diagonal in the local-orbital representation so that \(\langle \phi_i | z | \phi_j \rangle = \delta_{ij}z_i\).

We plot the bulk band structure of the TB Hamiltonian in Fig. 2(b). For the selected parameters the band gap is large compared to the band widths; in particular, the upper (unoccupied) band is quite flat. Next we compute the surface polarization of a ribbon cut from the 2D lattice, taking it to be ten unit cells thick along \(z\) and infinite along \(x\). For the atoms in the surface layers, the hoppings to the interior atoms are the same as those described above, while the hoppings to the vacuum side are set to zero. We used an equally spaced 60-point \(k_x\) grid. At each \(k_x\) the 20 \(\times\) 20 Hamiltonian is diagonalized, resulting in the band structure shown in Fig. 2(c). There are no obvious surface states, and in fact the result looks almost indistinguishable from a surface projection of the bulk band structure. The eigenfunctions \(|\psi_n(k_x)\rangle\) are expressed in the tight-binding ba-
sis as $|\psi_n(k_z)\rangle = \sum_j c_{nj}(k_z)|\chi_j(k_z)\rangle$, where the $|\chi_j(k_z)\rangle$ are the Bloch basis function formed as a Fourier sum at wavevector $k_z$ of atomic orbitals $|\phi_i\rangle$. From the ten occupied bands we construct the $10 \times 10$ position matrix $Z_{mn} = \langle \psi_m(k_z) | z | \psi_n(k_z) \rangle = \sum_j z_j c_{nj}(k_z) c^*_{mj}(k_z)$. Diagonalizing this matrix, we get ten eigenvalues $z_l(k_z)$ that can each be clearly associated with a particular unit cell layer, and ten eigenfunctions that are the HWFs. We label the HWF $|h_l(k_z)\rangle$, where $l$ is the layer index running from the bottom to the top of the ribbon.

Next we calculate $\gamma_{x,l}$, the Berry phase along $k_x$, for each $l$ using Eq. \(2\). Deep in the interior these Berry phases become equal to $\pi$ within numerical precision, while the Berry phases near the edge are slightly shifted away from $\pi$, leading to a nonzero surface polarization as shown in Fig. \(2\) (d).

The value of the surface polarization obtained from Eq. \(3\) is $P_x = \pm 2.1 \times 10^{-4} e$ for the top and bottom surfaces respectively. Similarly we can compute the surface polarizations for the left/right surfaces using a ribbon ten cells wide in $x$ and infinite along $z$. We obtain $P_x = \pm 4.7 \times 10^{-4} e$ along the left and right edges respectively. At the corners, the surface polarizations are directed head-to-head or tail-to-tail, as shown in Fig. \(2\) (a).

Given the values of the surface polarizations in the 2D model, we predict that the charge accumulation at the corner of a finite sample should equal the sum of the two adjacent surface polarizations, here $|P_x| + |P_z| = 6.8 \times 10^{-4} e$. To test this, we directly calculate the corner charge in a finite 2D sample, specifically a $10 \times 10$ supercell, large enough to ensure neutrality in the central region and in the middle of the edges of the sample. The corner charge is obtained by summing up the on-site charge differences, relative to the bulk, for atoms in the quadrant containing the corner. We find $Q_{\text{corner}} = 6.8 \times 10^{-4} e$ for the top left and bottom right corners, and $-6.8 \times 10^{-4} e$ for the other two corners, in agreement with our prediction from the computed surface polarizations.

We now consider a TB model of a generic III-V zincblende semiconductor, with GaAs as the prototypical example. The crystal structure is characterized by Ga-As zigzag chains running along \(\langle 110\rangle\). Although the crystal structure does not have inversion symmetry, the tetrahedral symmetry forbids a nonzero spontaneous polarization. We use tight-binding parameters from Ref. \[13\], in which is shown the bulk bandstructure and density of states. The unit cell contains two Ga and two As atoms, each with four $sp^3$ hybridized orbitals and four electrons, as shown in Fig. \(3\) (a). The position matrix is assumed to be diagonal and atom-centered in the basis of tight-binding orbitals. \[14\]

To describe the \(\langle 110\rangle\) surface, we construct a slab geometry as shown in Fig. \(3\) (a), and we henceforth label the Cartesian directions as shown there. That is, the surface, which is normal to $\hat{z}$, has zigzag chains running along $\hat{y}$. Since the two atoms making up these chains are inequivalent, we expect a surface polarization in the $\hat{x}$ direction. We take the slab to be eight unit cells thick; for the atoms in the surface layer, the hoppings to the atoms inside the slab are the same as in the bulk, while the hoppings to the vacuum side are set to zero. At each $(k_x,k_y)$ of the $100 \times 100$ grid in the surface BZ, the $128 \times 128$ Hamiltonian is diagonalized, and we obtain the band structure for the slab, shown in Fig. \(3\) (b). Surface states are evident as isolated bands.

Next, we diagonalize the $64 \times 64$ position matrices $Z(k_x,k_y)$ constructed from the eigenstates of the occupied bands. The eigenvalues, which are the $z$ coordinates of the HWF centers, can be clearly divided into groups, each consisting of four HWFs $j$ representing the four Ga-As bonds around an As atom, each group being associated with one of the 16 atomic layers $l$. In this case, it is more useful to calculate the Berry phase of each group of HWFs rather than of each single HWF \[3\].

As expected, the Berry phase in the $\hat{y}$ direction along the zigzag chain is found to be zero, but in the $\hat{x}$ direction it is nonzero for the HWF groups near the top and bottom surfaces of the slab. Thus, we confirm that there is a nonzero surface polarization $P_x$. We plot the difference between the Berry phase $\gamma_x$ of each group of HWFs and that for the bulk in Fig. \(3\) (c). By summing up the contri-
We sum up the site populations within the TB model with a 60-point $k$ grid along [111]. The onsite charge is the difference from the bulk value. The computed onsite charges are shown in the left half of Fig. 4(b), while the right half shows the corresponding results after averaging with a 60°-rotated version of itself. The surface charges decay rapidly into the bulk, leading to a neutral bulk state inside the nanowire. Also, a surface dipole density normal to the surface is clearly visible, especially in the orientationally averaged results. However, we are interested in the accumulation at the edges, which is obviously present in the unaveraged results in the left half of the figure. The edge charge is calculated by summing up the onsite charges in the wedge-shaped region illustrated in Fig. 4(b), using a weight of $1/2$ for atoms located on its radial edges. The total edge charge per trilayer is found to be $\pm 0.71e$, in agreement with the value predicted using the previously calculated surface polarization.

We emphasize that this numerical value is not intended to be realistic for GaAs. A more accurate estimate would require the use of an improved tight-binding model and treatment of surface relaxations and dielectric screening effects, or better, direct first-principles calculations. Our purpose here has been to show that the surface polarization as defined here correctly predicts edge charges. We note that an analysis based on maximally localized Wannier functions [15] is also possible. However, we believe our HWF-based approach is more natural, as the Wannier transformation is only done in the needed direction and no iterative construction is required.

We stress that the concept of surface polarization $\mathcal{P}$ is quite general, occurring whenever the surface symmetry is low enough. In some cases this can arise from a spontaneous symmetry-lowering surface relaxation or reconstruction, allowing “surface ferroelectricity” if it is switchable. In other cases, as for GaAs (110), the ideal surface space group already has low enough symmetry to allow a nonzero $\mathcal{P}$. This will occur quite generally for low-angle vicinal surfaces. The concept also applies to planar defects such as domain walls, stacking faults, and twin boundaries, and to heterointerfaces; if $\mathcal{P}$ is present within this plane, it may induce a line charge where the plane intersects the surface. Such edge and line charges are potentially observable using electric force microscopy [16], electron holography [17], or other experimental methods. Finally we note that the concept of surface polarization may become more subtle in the presence of orbital magnetization, which we have omitted from our considerations here.

In summary, we have formulated the concept of surface polarization, i.e., the dipole moment per unit area parallel to the surface, which can exist whenever the surface symmetry is low enough. Using TB models we have computed the surface polarizations for a 2D toy model and a generic III-V zincblende semiconductor, and shown that the predicted corner or edge charges are in good agree-
ment with direct calculations. We point out that surface and interface polarizations can be responsible for observable effects, and perhaps even desirable functionality, in a broad range of insulating materials systems.

We acknowledge helpful discussions with Hongbin Zhang, Jianpeng Liu and Massimiliano Stengel. This work is supported by NSF DMR-14-08838 and ONR N00014-11-1-0665.

[1] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
[2] R. Resta, Rev. Mod. Phys. 66, 899 (1994).
[3] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B 48, 4442 (1993).
[4] L. Bánya, P. Gilliot, Y. Z. Hu, and S. W. Koch, Phys. Rev. B 45, 14136 (1992).
[5] W. Wen, X. Huang, S. Yang, K. Lu, and P. Sheng, Nat. Mater. 2, 727 (2003).
[6] Y. Okada, M. Serbyn, H. Lin, D. Walkup, W. Zhou, C. Dhital, M. Neupane, S. Xu, Y. J. Wang, R. Sankar, F. Chou, A. Bansil, M. Z. Hasan, S. D. Wilson, L. Fu, and V. Madhavan, Science 341, 1496 (2013).
[7] K. Gupta, P. Mahadevan, P. Mavropoulos, and M. Lezai, Phys. Rev. Lett. 111, 077601 (2013).
[8] C. Sgarrovallo, M. Peressi, and R. Resta, Phys. Rev. B 64, 115202 (2001).
[9] X. Wu, O. Diéguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. 97, 107602 (2006).
[10] A. A. Soluyanov and D. Vanderbilt, Phys. Rev. B 83, 235401 (2011).
[11] M. Tahervinejad, K. F. Garrity, and D. Vanderbilt, Phys. Rev. B 89, 115102 (2014).
[12] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
[13] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974).
[14] J. Bennetto and D. Vanderbilt, Phys. Rev. B 53, 15417 (1996).
[15] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. 84, 1419 (2012).
[16] G. Valdrè, Imaging & Microscopy 8, 44 (2006).
[17] D. Wolf, H. Lichte, G. Pozzi, P. Prete, and N. Lovergine, Applied Physics Letters 98, 264103 (2011).