Density-Functional Theory of Polar Insulators

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We examine the density-functional theory of macroscopic insulators, obtained in the large-cluster limit or under periodic boundary conditions. For *polar* crystals, we find that the two procedures are not equivalent. In a large-cluster case, the exact exchange-correlation potential acquires a homogeneous "electric field" which is absent from the usual local approximations, and the Kohn-Sham electronic system becomes metallic. With periodic boundary conditions, such a field is forbidden, and the polarization deduced from Kohn-Sham wave functions is incorrect even if the exact functional is used. [S0031-9007(96)02156-4]

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Although the density-functional theory (DFT) introduced by Hohenberg, Kohn, and Sham [1,2] has become the standard method for first-principles calculations of the ground-state properties of solids, to our knowledge [3], the implications of applying DFT to infinite, insulating, crystals have not been fully appreciated. In part, this reflects the fact that the key theorems of DFT [1,2] were proved for arbitrarily large, but not infinite, systems. In the present Letter, we show that the exact DFT treatment of *polar* crystals (a) with the usual Born–von Karman (BvK) boundary conditions, or (b) from the macroscopic limit of large clusters, will generally give different macroscopic polarizations. Only (b) is correct.

Investigating the *response* of periodic insulators to a homogeneous electric field, we recently revealed [4] the polarization dependence of the exchange-correlation energy, and its consequences on the dielectric response. Aulbur, Jönsson, and Wilkins [5] quantified this effect for real materials, while Resta [6] discussed the origin of such a behavior in connection with long-range correlation effects. The present study emphasizes a more basic role of the polarization in DFT: careful handling of the polarization is mandatory for polar solids, even under zero electric field. In polar materials, the spontaneous polarization computed from the Kohn-Sham (KS) wave functions will be correct only if an exchange-correlation homogeneous electric field is allowed throughout the material, in which case the KS electronic system becomes *metallic*. This field will appear in the exact DFT treatment of a finite cluster but is forbidden when using BvK conditions. Approximate density functionals such as the local density approximation (LDA) and the generalized gradient approximation (GGA) always fail to yield an exchange-correlation electric field: within these approximations, using BvK boundary conditions or finite clusters incorrectly provide the *same* value of the polarization [7]. Any improvement to these functionals which retains a dependence only on the periodic density will be similarly flawed. We will exhibit our results for a one-dimensional model semiconductor.

The correct definition of a macroscopic crystal is clearly as the limit of a finite crystal of increasing size. Figure 1 shows schematically the total electrostatic potential $V_{\text{elec}} = V_e + V_N + V_{\text{appl}}$ in such a finite crystal, where V_e is the electrostatic potential due to the ground-state electron density, V_N is the potential due to the nuclei, and V_{appl} is an applied potential, created by an external short-circuited capacitor, that maintains equality of the electrostatic potential on the two sides [8]. The sum $V_{\text{ext}} = V_N + V_{\text{appl}}$ is referred to as the external potential. The total electrostatic potential in the bulk region is periodic and, crucially for a nonzero polarization, noncentrosymmetric. The potential just outside the surface is fixed by the electrostatic potential of the capacitor plates. The corresponding ground-state electron density is also shown. In the bulk region, it is periodic, with the same periodicity as the local potential [9]. Close to the surface, the density deviates from perfect periodicity, although this effect decreases exponentially with the distance from the surface [10].

The macroscopic polarization of such a finite solid is directly linked to the total surface charge [11,12]. Its value is equal to zero (modulo a half-quantum) if the crystal is centrosymmetric [12,13], but otherwise can have any value and must be calculated. For a long time the macroscopic polarization was only accessible from the surface charge and was a well-defined concept only for finite solids. Recent theoretical advances have shown that it can also conveniently be determined, up to a quantum, from a Berry phase of the correlated many-body wave function of the *bulk* [12–16]. Within this approach the macroscopic polarization appears as a bulk property and is unambiguously defined even for the infinite periodic solid, which is of practical interest in solid state *ab initio* calculations.

The breakthrough of King-Smith and Vanderbilt [14], leading to the modern theory of the polarization, was

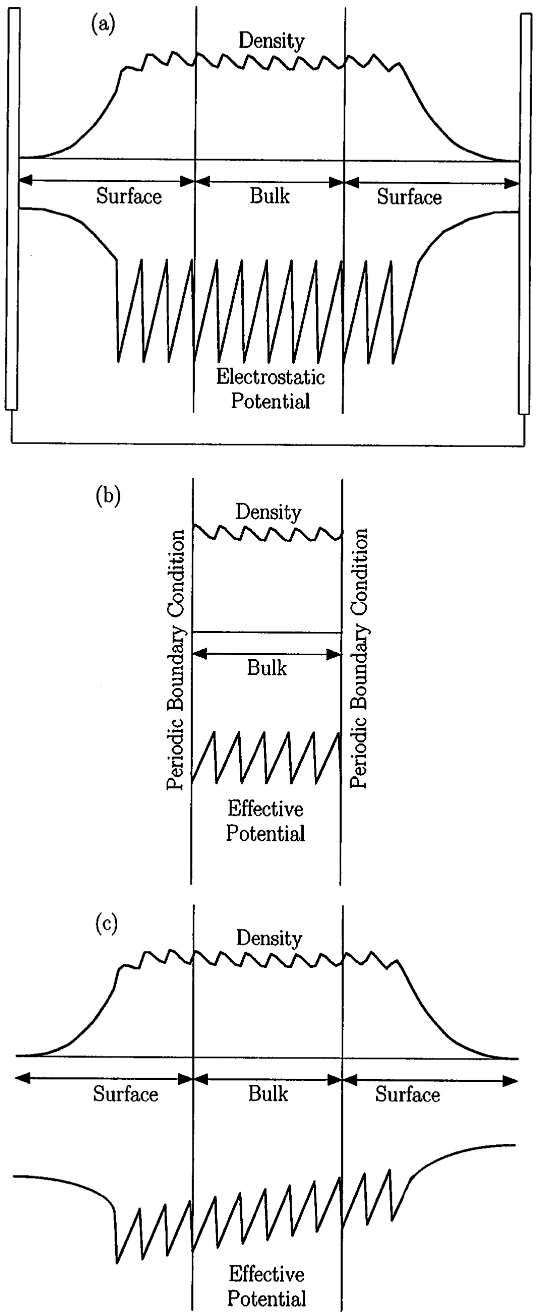

FIG. 1. (a) The local electrostatic potential (external plus Hartree) of an insulator, and the corresponding ground-state density. In the bulk region the potential is periodic. Short-circuited capacitor plates are also present. (b) The effective potential that, when used in Kohn-Sham equations, is able to reproduce the periodic part of the density shown in (a), under Born–von Karman periodic boundary conditions. The macroscopic polarization is not correct. (c) The effective potential that, when used in Kohn-Sham equations, is able to reproduce the density shown in (a), in all the regions of space. The macroscopic polarization is correct [in contrast to (b)].

actually carried out in the context of DFT. Later, they argued [12] that the Berry phase of the occupied KS wave functions possesses an exact physical meaning since the surface charge must be exactly reproduced within DFT [12]. We now show that the justification of Vanderbilt and King-Smith apply to exact DFT *only* when considering *finite* solids, and not when applying BvK periodic boundary conditions.

In the context of DFT, it is shown that the density $n(\mathbf{r})$ of the ground state of a system uniquely determines the external potential up to a constant. Following Kohn and Sham [2], one can introduce a fictitious system of noninteracting electrons in an effective potential $V_{\text{eff}} = V_{\text{ext}} + V_H + V_{\text{xc}}$ (where V_{xc} is the exchange correlation potential) that reproduces the ground-state electron density of the real system. In the particular case where *periodic boundary conditions* are imposed, although the KS effective potential V_{eff} is constrained to reproduce the correct *periodic* bulk density of the polar solid, there is no guarantee that it will reproduce the correct *polarization*, since this information is not contained in the criterion for the effective potential to be correct [17]. Such a periodic DFT is based only on the periodic part of the density, while the polarization is a completely independent quantity [4,6,13] that depends on the phase of the correlated wave functions. The polarization will be correct only in those solids where a fundamental symmetry (such as centrosymmetry) constrains the polarization, or where external parameters, such as the pressure, are fortuitously chosen.

We illustrate this for a one-dimensional model semiconductor [18]. In this model the electrostatic potential is periodic and asymmetric: $V_{\text{elec}}(x) = V_c \cos \frac{2\pi x}{a} + V_s \sin \frac{4\pi x}{a}$. A nonlocal self-energy operator, intended to mimic the relevant many-body effects, has the same nonlocal form as in Ref. [4]: $\Sigma(x, x', \omega) = \frac{f(x)+f(x')}{2} g(|x - x'|)$ where $f(x) = F_0[1 - \cos \frac{2\pi x}{a}]$ is a negative function with the periodicity of one unit cell and $g(y)$ is a normalized Gaussian of width w.

First, the Schrödinger equation containing the self-energy operator is solved by direct diagonalization using a plane-wave basis set. The density is deduced from the sum of the squares of the eigenfunctions. From this result, using standard iterative optimization techniques, we construct an *exact* density-functional theory by determining the local potential $V_{\text{eff}}(x)$ which, when filled with *noninteracting* electrons (no self-energy operator), reproduces the same electron density as in the self-energy calculation. Figure 2 presents the function $V_{\text{elec}}(x)$, as well as the density $n(x)$, and the effective potential $V_{\text{eff}}(x)$, for the following set of parameters: $a_0 = 4$ a.u., $V_c = V_s = 2.72$ eV, $F_0 = -4.08$ eV, $w = 2$ a.u.

Using the Berry-phase approach [13,14], we then compute the polarization [19]. In the self-energy calculation, the polarization is 22.68×10^{-3} electrons with respect to the centrosymmetric system with $V_s = 0$, while that calculated from the Berry phase of the Kohn-Sham wave functions is 21.99×10^{-3} electrons. The two polarizations differ by 3%, well outside the calculational error bar. This value may be taken as an order of magnitude estimation of the effect in real materials, and is

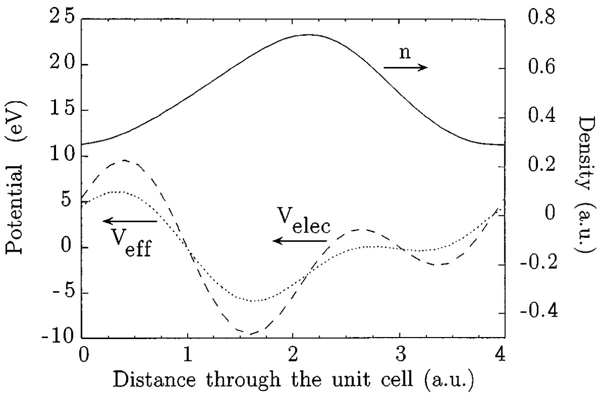

FIG. 2. The electrostatic potential $V_{\mathrm{elec}}(x)$, the electron density $n(x)$, and the Kohn-Sham effective potential $V_{\mathrm{eff}}(x)$ of the model one-dimensional semiconductor are shown when periodic boundary conditions are imposed [corresponding to Fig. 1(b)]. The Kohn-Sham electrons correctly reproduce the electron density, but not the macroscopic polarization.

compatible with the observed (and often satisfactory) accuracy of LDA polarization calculations for real ferroelectric materials [20].

The deficiency in the periodic-boundary approach, reflected in the Berry phase of the KS wave functions and hence in the polarization, is that the exchange-correlation potential is prevented from having a component which is linear in space [21]. The KS theorem demonstrates that there is only one periodic effective potential V_{eff} that reproduces a particular periodic density. However, once an additional linear component is allowed, there exists an infinite family of KS potentials that gives the same periodic density but different polarizations [4]. Imposing BvK conditions on the potential thus arbitrarily constrains the polarization to a specific, usually incorrect, value. This restriction does not apply for the finite cluster, where application of the KS theorem shows that there exists a unique effective potential that, when used in the effective Hamiltonian, will generate the exact ground-state density *everywhere:* not only in the bulk region (as in the BvK case), but *also* in the surface region, resulting in the correct polarization. Figure 1(c) sketches the behavior of such an effective potential. The linear part is necessary to yield the correct polarization in polar crystals. This "exchange-correlation electric field" originates in the ultra nonlocal dependence of the exchange-correlation energy in the surface charge pointed out in Ref. [4].

In the small cluster shown in Fig. 1(c), the magnitude of the exchange-correlation field is approximately independent of the cluster size, since the polarization correction relative to periodic DFT is constant. As the cluster is made larger, a point will be reached where the variation in potential from one side of the cluster to the other, due to the homogeneous exchange-correlation electric field, reaches the DFT band gap of the material. Beyond this point, the KS electronic system is *metallic* and the band edges will "pin"

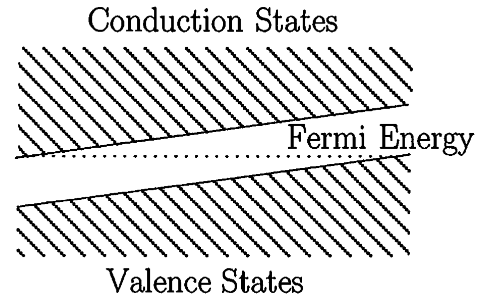

FIG. 3. For sufficiently large clusters, the exchange-correlation field will cause band overlap and hence metallization. Further increase in cluster size leaves the band edges pinned as shown, and charge transfer occurs between the two surfaces.

the effective potential (Fig. 3). As the cluster is made still larger, charge will flow freely from one face to the other in order to maintain the correct macroscopic polarization. The magnitude of the homogeneous electric field will now change with the size of the cluster in order to maintain the potential drop: in the limit of large cluster size, the effective homogeneous electric field will be infinitesimally small, although nonzero. As mentioned in Ref. [22], an infinite system cannot sustain a finite homogeneous electric field in its ground state. Here, an infinitesimal field appears naturally in the DFT treatment of polar solids.

There is a strong similarity between this behavior and that of a system of two distant, different, open-shell atoms [23], in which the exact exchange-correlation potential exhibits a long-range spatial variation to align the Kohn-Sham eigenvalues. There is also a connection with the DFT metal/insulator paradox [24] in which an insulating system may be described as metallic in DFT.

In summary, for a polar insulator, when Born–von Karman periodic boundary conditions are used, the polarizations calculated from the Berry phase of the Kohn-Sham wave functions and from the Berry phase of the correlated wave function will differ, because the DFT effective potential is prevented from acquiring a linear part. When a large cluster is used for the DFT calculation, a homogeneous effective exchange-correlation "electric field" develops in order to correctly reproduce the polarization. The Kohn-Sham system becomes metallic.

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[8] For the simplicity of the argument, we imagine that the capacitor is a classical device, in which case the analysis of electrostatics performed in Ref. [6] applies.

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