Macroscopic electrical polarization of materials
(disordered and crystalline)

Raffaele Resta
Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I–34014 Trieste, Italy
and CNR-INFM DEMOCRITOS National Simulation Center, via Beirut 2, I–34014 Trieste, Italy
E-mail: resta@democritos.it

Abstract. I provide here a comprehensive presentation of the so called “modern theory of polarization”, based on a Berry phase. This theory is implemented as a standard option in most electronic-structure codes for both crystalline and noncrystalline materials, and is routinely used whenever features of the macroscopic electrical polarization of materials are addressed. Several reviews of the modern theory exist in the literature; with respect to them, the present work has important elements of novelty. In this work I present a formal derivation, starting from the many-body wavefunction at the most general level, and eventually specialising to the case of single-determinant wavefunctions for either disordered or crystalline materials.

1. Introduction
The macroscopic polarization is a central concept in any phenomenological description of dielectric media [1]. Intuitively, it should be an intensive vector quantity carrying the meaning of electric dipole moment per unit volume. Despite such centrality, most textbooks addressing the polarization of a condensed system provide a flawed definition, not implementable in practical computations.

A change of paradigm was proposed in the early 1990s by Resta [2]; the so-called “modern theory of polarization”, based on a Berry phase, was founded by King-Smith and Vanderbilt soon afterwards [3, 4]. At its foundation, the modern theory was limited to a crystalline system in a mean-field—either density-functional-theory (DFT) or Hartree-Fock (HF)—framework. Later, the theory was extended to correlated and/or disordered systems [5, 6]. By now, most electronic-structure codes for condensed-matter systems, either crystalline [7, 8, 9, 10] or noncrystalline [11], implement the Berry phase as a standard option.

The modern theory avoids addressing “polarization itself”, quite in agreement with the experiments, which invariably measure polarization differences. In fact, the modern paradigm [2] addresses differences in polarization between two states of the material that can be connected by an adiabatic switching process. The time-dependent Hamiltonian is assumed to remain insulating at all times, and the polarization difference is then equal to the time-integrated transient macroscopic current that flows through the insulating sample during the switching process:

$$\Delta P = P(\Delta t) - P(0) = \int_0^{\Delta t} dt \, j(t).$$

(1)
In the adiabatic limit $\Delta t \to \infty$ and $j(t) \to 0$, while $\Delta P$ stays finite. Addressing currents (instead of charges) explains the occurrence of phases of the wavefunctions (instead of square moduli) in the modern theory. I anticipate that eventually the time integration in Eq. (1) will be eliminated, leading to a two-point formula involving only the initial and final states.

Several comprehensive presentations, based on somewhat different formulations, have appeared in the literature \cite{4, 12, 13, 14, 15}. With respect to them, this work introduces several novelties. For instance, the adiabatic-connection formula as given in Eq. (8), in terms of a many-body Berry curvature, is new. Also new are the introduction of the total (nuclear plus electronic) phase, Eq. (14) and following related ones, and the thorough discussion of the polarization “quantum” in disordered vs. crystalline systems. Throughout this work we emphasize the discrete Berry-phase formulation, arriving at the continuous $k$-space formula of King-Smith and Vanderbilt \cite{3} only at the very end, Eq. (26).

As presented here, the modern theory only addresses the problem of computing electric polarization in a vanishing macroscopic electric field. It is therefore suitable to studying ferroelectricity (spontaneous polarization), piezoelectricity (strain-induced polarization), and lattice infrared activity and dielectric response (displacement-induced polarization). Further developments \cite{16, 17}, reviewed in Refs. \cite{14, 15} and not addressed in the present work, extend the theory to the problem of computing polarization in a finite electric field, such as to address permittivity (field-induced polarization) as well. The modern theory can be equivalently formulated in terms of localized Wannier orbitals, apparently (and only apparently) free from any phase information. The Wannier formulation, not addressed in this work, is thoroughly presented e.g. in Refs. \cite{4, 14}.

2. Macroscopic polarization from the ground-state wavefunction

We start at a very general level, including in the treatment even correlated and/or noncrystalline many-electron systems. We adopt atomic Hartree units throughout. Suppose we have $N$ electrons in a cubic box of volume $L^3$, with a many-body Hamiltonian

$$
\hat{H} = \frac{1}{2} \sum_{i=1}^{N} |\mathbf{p}_i|^2 + \hat{V},
$$

and eigenfunctions $|\Psi_n\rangle$, normalized in the hypercube of volume $L^{3N}$. In Eq. (2) the potential $\hat{V}$ includes one-body and two-body (electron-electron) contributions. As usual in condensed-matter theory, we adopt periodic Born-von-Kármán boundary conditions over each electron coordinate $\mathbf{r}_i$ independently, whose Cartesian components $r_{i,\alpha}$ are then equivalent to the angles $r_{i,\alpha}/(2\pi L)$. The potential $\hat{V}$ enjoys the same periodicity, which implies that the electric field averages to zero over the sample.

We generalize Eq. (2) by including a “flux” or “twist” by means of a parameter $\kappa$, having the dimension of an inverse length

$$
\hat{H}(\kappa) = \frac{1}{2} \sum_{i=1}^{N} |\mathbf{p}_i + \kappa|^2 + \hat{V},
$$

such that the eigenvalues and eigenvectors acquire a $\kappa$ dependence. It is then expedient to evaluate the $\kappa$-gradient of the ground eigenstate $|\Psi_0(\kappa)\rangle$ at $\kappa = 0$, for which we introduce the simplified notation $|\nabla_\kappa \Psi_0\rangle$. Straightforward perturbation theory yields:

$$
|\nabla_\kappa \Psi_0\rangle = \sum_{n \neq 0} \langle \Psi_n | \hat{p} | \Psi_0 \rangle \frac{\langle \Psi_n | \hat{p} | \Psi_0 \rangle}{E_0 - E_n}.
$$
Suppose that the nuclei are at sites $\mathbf{R}_m$ with charges $Z_m$; when they are adiabatically displaced the potential $V$ becomes time-dependent and the macroscopic electrical current (nuclear plus electronic) entering Eq. (1) is

$$ j(t) = j^{\text{nucl}}(t) + j^{\text{el}}(t) = \frac{1}{L^3} \left[ \sum_m Z_m \frac{d\mathbf{R}_m}{dt} - \langle \Psi(t) | \hat{p} | \Psi(t) \rangle \right].$$

Notice that the overall charge neutrality of the system ($N = \sum_m Z_m$) is essential for dealing with dipolar properties.

If the system is initially in its ground state $|\Psi_0\rangle$, then the electronic current flowing through the sample is cast, in terms of the adiabatic instantaneous eigenstates, as

$$ j^{\text{el}} = -i \frac{L^3}{3} \sum_{n \neq 0} \frac{\langle \partial_t \Psi_0 | \nabla_{\kappa} \Psi_n \rangle \langle \Psi_n | \hat{p} | \Psi_0 \rangle}{E_n - E_0} + \text{c.c.},$$

where “c.c.” stays for complex conjugate, $\partial_t = \partial / \partial t$, and the time-dependence is implicit. Notice that in Eq. (6) it is essential that the system maintains a finite gap between the ground and the first excited states, i.e. that the system is insulating at all times.

Comparison with Eq. (4) allows to formally eliminate the sum over the excited states, and recasting $j^{\text{el}}$ as a pure ground-state property:

$$ j^{\text{el}} = -i \frac{L^3}{3} \left[ \langle \partial_t \Psi_0 | \nabla_{\kappa} \Psi_0 \rangle - \langle \nabla_{\kappa} \Psi_0 | \partial_t \Psi_0 \rangle \right] = \frac{2}{L^3} \text{Im} \langle \partial_t \Psi_0 | \nabla_{\kappa} \Psi_0 \rangle .$$

If we regard the adiabatic instantaneous ground eigenstate of Eq. (3) as a function of the four-dimensional variable $(t, \kappa)$, then the rhs of Eq. (7) is a “Berry curvature” [13] (times a constant factor), evaluated at $\kappa = 0$ and at an arbitrary $t$.

The electronic contribution to the macroscopic polarization of any insulating many-electron system, Eq. (1), is therefore defined in terms of the adiabatic instantaneous ground eigenstate; the total polarization difference is

$$ \Delta \mathbf{P} = \int_0^{\Delta t} dt \ j^{\text{nucl}}(t) + \frac{2}{L^3} \text{Im} \int_0^{\Delta t} dt \ \langle \partial_t \Psi_0 | \nabla_{\kappa} \Psi_0 \rangle,$$

where the (classical) nuclear term will be discussed below. The definition given in Eq. (8), based on adiabatic connection, is very compact and elegant. However this form is not very useful for actual computations because of two reasons: (i) it requires an integration over all the intermediate quantum states (between the initial and final one); (ii) it requires a sum over all the excited states, if Eq. (4) is actually used in Eq. (8). Both drawbacks are eliminated by the transformation provided in the following Section [6, 13].

3. Single-point Berry phase

We start defining the three many-body operators $\hat{U}_\alpha = \exp(i \frac{2\pi}{L^3} \sum_i r_i, \alpha)$, so-called “twist” operators; they are unitary and Born-von-Kármán periodic. Their ground-state expectation values $\langle \Psi_0 | \hat{U}_\alpha | \Psi_0 \rangle$ are complex numbers whose modulus is no larger than 1, and whose phase

$$ \gamma^{(\text{el})}_\alpha = \text{Im} \ln \langle \Psi_0 | \hat{U}_\alpha | \Psi_0 \rangle$$

is the “single-point” electronic Berry phase [13] at an arbitrary $t$. Notice that $|\Psi_0\rangle$ is the ground adiabatic eigenstate of Eq. (3) at $\kappa = 0$: this coincides with the ground eigenstate of the (less exotic) Eq. (2).
Ab initio Simulation of Crystalline Solids: History and Prospects

By substitution it is easy to verify that \( \hat{U}_\alpha |\Psi_0\rangle \) is the lowest eigenstate of Eq. (3) for \( \kappa = (-\frac{2\pi}{L}, 0, 0) \), and analogously for the other Cartesian components. It is then tempting to identify, in the large-\( L \) limit, \( |\nabla_{\kappa_0} |\Psi_0\rangle \simeq -\frac{L}{2\pi} (\hat{U}_\alpha - 1)|\Psi_0\rangle \), but this would be incorrect owing to an arbitrary phase factor in the eigenstates at different \( \kappa \). This drawback is fixed by the so-called “covariant derivative” \[\kappa\], writing

\[
|\nabla_{\kappa_0} |\Psi_0\rangle = -\frac{L}{2\pi} \left( \frac{\hat{U}_\alpha |\Psi_0\rangle}{\langle \Psi_0 |\hat{U}_\alpha |\Psi_0\rangle} - |\Psi_0\rangle \right),
\]

(10)
correct to leading order in \( 1/L \).

Next, we address the time derivative of Eq. (9)

\[
\frac{d\gamma^{(el)}_\alpha}{dt} = \text{Im} \left( \frac{\langle \partial_t |\Psi_0\rangle \hat{U}_\alpha |\Psi_0\rangle + \langle |\Psi_0\rangle \hat{U}_\alpha \partial_t |\Psi_0\rangle}{\langle |\Psi_0\rangle \hat{U}_\alpha |\Psi_0\rangle} \right) = 2 \text{Im} \left( \frac{\langle \partial_t |\Psi_0\rangle \hat{U}_\alpha |\Psi_0\rangle - \langle |\Psi_0\rangle \hat{U}_\alpha |\Psi_0\rangle}{\langle |\Psi_0\rangle \hat{U}_\alpha |\Psi_0\rangle} \right),
\]

(11)
by substituting Eq. (10) into Eq. (11) we get

\[
\frac{d\gamma^{(el)}_\alpha}{dt} = -\frac{4\pi}{L} \text{Im} \langle \partial_t |\Psi_0\rangle |\nabla_{\kappa} |\Psi_0\rangle. \tag{12}
\]

The (classical) nuclear contribution can also be cast in terms of a phase, by defining

\[
\gamma^{(nucl)}_\alpha = \text{Im} \ln e^{-i\frac{2\pi}{L} \sum_m Z_m R_{m,\alpha}} = -\frac{2\pi}{L} \sum_m Z_m R_{m,\alpha} \quad \text{(modulo } 2\pi\text{)}. \tag{13}
\]

The total (nuclear plus electronic) phase is then, from Eq. (9)

\[
\gamma_\alpha = \text{Im} \ln e^{-i\frac{2\pi}{L} \sum_m Z_m R_{m,\alpha}} + \text{Im} \ln \left| \langle \Psi_0 | e^{i\frac{2\pi}{L} \sum m Z_m R_{m,\alpha}} |\Psi_0\rangle \right| = \text{Im} \ln \left| \langle \Psi_0 | e^{i\frac{2\pi}{L} \sum m Z_m R_{m,\alpha} + \sum m r_{i,\alpha}} |\Psi_0\rangle \right|, \tag{14}
\]
and its time derivative is, from Eqs. (12) and (13),

\[
\frac{d\gamma_\alpha}{dt} = -\frac{2\pi}{L} \left[ \sum_m Z_m \frac{dR_{m,\alpha}}{dt} + 2 \text{Im} \langle \partial_t |\Psi_0\rangle |\nabla_{\kappa} |\Psi_0\rangle \right]. \tag{15}
\]

4. Two-point formula and the polarization “quantum”

Comparison of Eq. (15) with Eqs. (5) and (8) leads to

\[
\Delta P_\alpha = \frac{1}{2\pi L^2} \int_0^{\Delta t} dt \frac{d\gamma_\alpha}{dt} = -\frac{1}{2\pi L^2} \left[ \gamma_\alpha(\Delta t) - \gamma_\alpha(0) \right] = -\frac{1}{2\pi L^2} \Delta \gamma_\alpha. \tag{16}
\]

We thus arrived at a two-point formula, where the electronic contribution to the polarization difference between two states of the same material (connected by an adiabatic switching process) is cast in terms of the difference between the two Berry phases of the initial and final states. Such phases, in turn, only depend on the ground-state many-body wavefunctions and on the corresponding nuclear geometries, from Eq. (14).

Given that every phase is defined modulo \( 2\pi \), the value of \( \Delta P_\alpha \) in Eq. (16) is arbitrary modulo \( 1/L^2 \). This is the tradeoff one has to pay when switching from the adiabatic-connection formula, Eq. (8)—where no such arbitrariness exists—to the two-point formula, Eq. (16).

4
Since we are interested in the large-system limit, where the “quantum” vanishes, the two-point formula is apparently useless. This is not the case, and in fact Eq. (16) is routinely used for evaluating polarization differences in both disordered and crystalline materials. More will be said about this below. For the time being, let me point out that the $L \to \infty$ limit is not actually needed; for an accurate description of a given material, it is enough to assume a finite $L$, actually larger than the relevant correlation lengths in the material. For any given length, the polarization “quantum” $1/L^2$ sets an upper limit to the magnitude of a polarization difference accessible via the two-point formula, Eq. (16). The larger are the correlation lengths, the smaller is the accessible $\Delta P$. Whenever needed, the drawback may be overcome by splitting $\Delta t$ in Eq. (8) into several smaller time intervals, and by using the two-point formula for each of them. We anticipate that in the crystalline case the “quantum” issue is dramatically simplified by lattice translational invariance.

5. Single-determinant wavefunctions

We now specialize to the case where the $N$-electron ground state $|\Psi_0\rangle$ is a Slater determinant of $N/2$ double-occupied single-particle orbitals $\varphi_j(r)$. This applies to either HF or DFT cases, where the orbitals are either the HF or the Kohn-Sham ones.

Starting from the key definition of Eq. (9) we notice that the state $\hat{U}_\alpha|\Psi_0\rangle$ is the Slater determinant built from the modified orbitals $\tilde{\varphi}_j(r) = \exp(i2\pi r/\alpha)|\varphi_j(r)\rangle$, and therefore the matrix element in Eq. (9) is the overlap between two single-determinant wavefunctions. According to a well known theorem such overlap is equal to the determinant of the overlap matrix between the corresponding spinorbitals. In our case, reckoning for double occupancy and factorization, we may write

$$\langle \Psi_0| \hat{U}_\alpha |\Psi_0\rangle = (\det S_\alpha)^2,$$

where $S_\alpha$ is the $N/2 \times N/2$ overlap matrix between spatial orbitals

$$S_{\alpha,jj'} = \langle \varphi_j | \tilde{\varphi}_{j'} \rangle = \langle \varphi_j | e^{i2\pi r/\alpha} | \varphi_{j'} \rangle.$$

We thus arrive at the Slater-determinant form of Eq. (14)

$$\gamma_\alpha = \frac{2\pi}{L} \left[ -\sum_m Z_m R_{m,\alpha} + 2 \text{Im} \ln \det S_\alpha \right].$$

This expression, inserted into Eq. (16), provides the two-point formula routinely used in Car-Parrinello simulations [19] for noncrystalline systems, whenever polarization features are addressed [20], and is implemented as a standard option within Car-Parrinello codes [11]. We notice that the “quantum” problem is irrelevant here, since $\Delta t$ is a Car-Parrinello time step (a few a.u.), during which the polarization varies by a tiny amount, much smaller than the quantum $1/L^2$ (the typical size of a large simulation cell is $L \approx 50$ a.u.).

In principle, Eq. (19) could be used as it stands even for crystalline systems. It is however much more convenient to exploit translational symmetry, by identifying the orbitals $\varphi_j(r)$ entering Eq. (18) with the Bloch orbitals of the occupied bands, leading to a special form of Eq. (19). This is discussed in the forthcoming Section.

6. Crystalline insulators

Let us assume, for the sake of simplicity, a simple cubic lattice of lattice constant $a$. Then the Born-von-Kármán period $L$ is an integer multiple of the lattice constant: $L = Ma$, where $M \to \infty$ in the large-system limit. The most general crystal structure can be considered by means of a simple coordinate transformation [4].
The allowed Bloch vectors are discrete
\[ \mathbf{k}_{s_1,s_2,s_3} = \frac{2\pi}{Ma}(s_1, s_2, s_3), \quad s_\alpha = 0, 1, \ldots, M-1, \] (20)
and the corresponding Bloch orbitals are \( \psi_n(\mathbf{k}_{s_1,s_2,s_3}; \mathbf{r}) = e^{i\mathbf{k}_{s_1,s_2,s_3} \cdot \mathbf{r}} u_n(\mathbf{k}_{s_1,s_2,s_3}; \mathbf{r}) \). The overlap matrix of Eq. (18) becomes then
\[ S_{\alpha,j,j'} \rightarrow \frac{1}{M^3} \int_0^L dx \int_0^L dy \int_0^L dz \psi^*_{n}(\mathbf{k}; \mathbf{r}) e^{i\frac{2\pi a}{Ma} \cdot \mathbf{r}} \psi'_{n'}(\mathbf{k}'; \mathbf{r}) \]
\[ = \frac{1}{M^3} \int_0^L dx \int_0^L dy \int_0^L dz u^*_{n}(\mathbf{k}; \mathbf{r}) e^{i(\mathbf{k}' - \mathbf{k} + \frac{2\pi a}{Ma}) \cdot \mathbf{r}} u_{n'}(\mathbf{k}' ; \mathbf{r}), \] (21)
where \( \mathbf{k} \) and \( \mathbf{k}' \) must be chosen within the discrete set. The \( 1/M^3 \) factor owes to the fact that \( |\Psi_0\rangle \) is normalized in the hypercube of volume \( L^3N \), while the Bloch orbitals \( \psi_n \) and \( u_n \) are normalized in the cube of volume \( a^3 \). For given \( \mathbf{k} \) and \( \mathbf{k}' \) the size of the matrix on the rhs of Eq. (21) is \( n_b \) (the number of double-occupied bands), while the \( \mathbf{k} \) and \( \mathbf{k}' \) arguments run over \( M^3 \) discrete values. In fact, the total number of electrons in the Born-von-Kármán box (and the size of the Slater determinant) is \( N = 2n_b M^3 \).

The overlap matrix in Eq. (21) is very sparse. Focussing, without loss of generality, on the \( x \)-component (\( \alpha = 1 \)), and writing explicitly \( \mathbf{k} = \mathbf{k}_{s_1,s_2,s_3} \) and \( \mathbf{k}' = \mathbf{k}'_{s'_1,s'_2,s'_3} \), its only nonzero elements are those with \( s_1 = s'_1 + 1, s_2 = s'_2, \) and \( s_3 = s'_3 \). With the usual definition of the scalar product between \( u_n \) orbitals
\[ \langle u_n(\mathbf{k}) | u_{n'}(\mathbf{k}') \rangle = \int_{\text{cell}} d\mathbf{r} u^*_n(\mathbf{k}; \mathbf{r}) u_{n'}(\mathbf{k}' ; \mathbf{r}), \] (22)
these nonzero elements can be rewritten as
\[ S_{nn'}(\mathbf{k}_{s_1+1,s_2,s_3}, \mathbf{k}_{s_1,s_2,s_3}) = \langle u_n(\mathbf{k}_{s_1+1,s_2,s_3}) | u_{n'}(\mathbf{k}_{s_1,s_2,s_3}) \rangle. \] (23)
Owing to such sparseness, the determinant of the large matrix \( S_x \) (of size \( N/2 = n_b M^3 \)) in Eq. (19) factorizes into the product of \( M^3 \) determinants of the small matrices \( S(\mathbf{k}, \mathbf{k}') \) (of size \( n_b \) each).

In the crystalline case it proves convenient to define the Berry phase \( \gamma^{(\text{crys})}_\alpha \), differing by a factor \( 1/M^2 \) from the \( \gamma_\alpha \) used so far. Eqs. (16) and (19) become then
\[ \Delta P_\alpha = -\frac{1}{2\pi a^2} \Delta \gamma^{(\text{crys})}_\alpha. \] (24)
\[ \gamma^{(\text{crys})}_x = -\frac{2\pi}{a} \sum_\ell Z_\ell \tau_\ell x + \frac{2}{M^2} \text{Im} \ln \prod_{s_1,s_2,s_3=0}^{M-1} \det S(\mathbf{k}_{s_1+1,s_2,s_3}, \mathbf{k}_{s_1,s_2,s_3}) \]
\[ = -\frac{2\pi}{a} \sum_\ell Z_\ell \tau_\ell x - \frac{2}{M^2} \sum_{s_2,s_3=0}^{M-1} \text{Im} \ln \prod_{s_1=0}^{M-1} \det S(\mathbf{k}_{s_1,s_2,s_3}, \mathbf{k}_{s_1+1,s_2,s_3}), \] (25)
where \( \tau_\ell \) are the nuclear coordinates in the unit cell. Analogous expressions hold for the \( y \)- and \( z \)-components.

We notice that the \( u_n(\mathbf{k}) \) orbitals entering \( S \), Eq. (23), can be chosen with arbitrary phase factors (choice of the “gauge”), but these factors cancel out in Eq. (25), leaving no arbitrariness. Even more, Eq. (25) is invariant by unitary transformations of the occupied orbitals at a given
Therefore the electronic term in $\gamma_{\alpha}^{(\text{cris})}$ is a global property of the occupied manifold as a whole; this is useful when the band numbering is nonunique (e.g. in the case of band crossings).

In the $M \to \infty$ limit the $k$-point mesh becomes dense. If the gauge is chosen in such a way that the overlap matrix $S_{n,m}(k,k') = \langle u_n(k) | u_m(k') \rangle$ is a differentiable function of its arguments, Eq. (25) converges to a reciprocal-cell integral. In fact it can be shown [3, 4, 13] that

$$
\lim_{M \to \infty} \frac{1}{M^2} \sum_{s_2,s_3=0}^{M-1} \text{Im} \ln \prod_{s_1=0}^{M-1} \det S(k_{s_1+s_2,s_3}, k_{s_1+1,s_2,s_3})
= \frac{i a^2}{(2\pi)^2} \int dk \frac{\partial}{\partial k_x} \sum_{n=1}^{n_b} S_{nn}(k,k') \bigg|_{k'=k} = \frac{i a^2}{(2\pi)^2} \int dk \sum_{n=1}^{n_b} \langle u_n(k) | \frac{\partial}{\partial k_x} u_n(k) \rangle. \quad (26)
$$

The nuclear term in Eq. (25) is arbitrary by $2\pi$, while the reciprocal-cell integral in Eq. (26) is a (continuous) Berry phase, which can be shown [3, 4] to be gauge-invariant modulo $2\pi$ as well. Then the two-point formula, Eq. (24) defines $\Delta P$ modulo the polarization “quantum” $1/a^2$, large enough to be harmless in most practical circumstances.

The discrete expression of Eq. (25) is the one actually implemented (at finite $M$) into the available electronic-structure codes for crystalline systems [7, 8, 9, 10]. Since “Im ln” amounts to evaluating the phase of the complex number on its right, the electronic term in Eq. (25) is the average (over the $k_y k_z$ plane) of an $M$-point discrete Berry phase [13]. Caution about the polarization “quantum” is in order for the discrete case: if each of the $M$-point Berry phases in the sum is chosen with arbitrary modulo $2\pi$ freedom, then $\gamma_{\alpha}^{(\text{cris})}$ is unavoidably arbitrary modulo $4\pi/M^2$. A more clever choice is possible, and actually performed, as follows. One starts choosing arbitrarily one of the possible (modulo $2\pi$) values for the first term in the sum ($s_2 = 0$ and $s_3 = 0$); for the remaining terms, it is possible to impose that nearest-neighbor phases differ by much less than $2\pi$ (if the mesh is dense enough). This choice is unique, and eliminates any residual arbitrariness, corresponding to the discrete average of a continuous function of $k_y k_z$, as indeed in Eq. (26). By this token the discrete Berry-phase formula, Eq. (25), leads to the “quantum” value $1/a^2$ (independent of $M$ and $L$), indeed identical to the continuous one.

### 7. Conclusions

The final expression in Eq. (26) is the electronic Berry phase which historically provided the foundation of the “modern theory of polarization”. When inserted into Eqs. (24) and (25) it leads the (by now famous) King-Smith and Vanderbilt formula [3] for the macroscopic polarization of a crystalline insulator in a mean-field framework (either HF or DFT) [14, 15]. The present work only deals, for the sake of simplicity, with a simple cubic lattice of constant $a$, while the expression for the most general lattice obtains from a simple coordinate transformation [4].

The comprehensive presentation of the modern theory of polarization given here follows a path which is different from the historical one. In fact, the discrete form of Eq. (25) was proposed in the early literature [3, 4, 12] only as a convenient numerical recipe for implementing the corresponding continuous $k$-space form, while ensuring numerical gauge invariance. Later, it was discovered [6, 13] that the discrete formula is indeed more fundamental than the continuous one, since it can be regarded as the special case of a very general formula, addressing even noncrystalline and/or correlated insulating materials.

Based on this finding, the modern theory of polarization is presented here in “reverse” with respect to the historical development: we start from the very general formula and eventually we specialize it to the case of a crystalline insulator in a mean-field framework, thus arriving at the famous 1993 formula [3] only at the end of this work. The general formula, originally published in Ref. [6], is presented here in a very compact and elegant way, Eqs. (14) and (16), including
a novelty: the nuclear contribution to macroscopic polarization enters the theory on the same
ground as the electronic one, by means of a very compact phase form, Eq. (14).

The modern theory of polarization has been a genuine change of paradigm in condensed-
matter theory [14, 15], and is nowadays implemented in many electronic structure codes as a
standard option in order to study ferroelectricity, piezoelectricity, and infrared activity. As
for ferroelectricity, the experimental values of the spontaneous polarization in ferroelectric
perovskite oxides are known since the 1950s; no quantum-mechanical evaluation (or even
estimate) was possible, as a matter of principle, before the advent of the modern theory. The first
calculation ever, performed within first-principle DFT for KNbO$_3$, appeared in 1993 [21] and
was in agreement with the experiment within 5%. Subsequent calculations for other materials,
within either DFT or HF [22], showed a similar kind of agreement. A review of the recent
ferroelectrics literature can be found in Ref. [23].

Here we have emphasized concepts and formal results, while also addressing some key details
(such as the “quantum” issue) for practical implementations in both disordered and crystalline
systems. The former case concerns Car-Parrinello simulations, while the latter concerns self-
consistent band-structure calculations. Because of space limitations, we have not
covered a couple of important aspects of the modern theory: its relationship to Wannier orbitals, and its
extension to the case where a finite electrical field is present in the material. Both aspects are
reviewed e.g. in Refs. [14, 15].

Acknowledgments
Work supported by the ONR grant N00014-07-1-1095.

References
[1] Landau L D and Lifshitz E M 1984 Electrodynamics of Continuous Media (Oxford: Pergamon)
[2] Resta R 1992 Ferroelectrics 136 51
[3] King-Smith R D and Vanderbilt D 1993 Phys. Rev. B 47 1651
[4] Resta R 1994 Rev. Mod. Phys. 66 899
[5] Ortiz G and Martin R M 1994 Phys. Rev. B 43 14202
[6] Resta R 1998 Phys. Rev. Lett. 80 1800
[7] http://www.abinit.org/
[8] http://www.crystal.unito.it/
[9] http://cms.mpi.univie.ac.at/vasp/
[10] http://www.pwscf.org
[11] http://www.cpmd.org/
[12] Resta R 1996 Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials (Lecture
Notes in Chemistry vol 67) ed C Pisani (Berlin: Springer) p 273
[13] Resta R 2000 J. Phys.: Condens. Matter 12 R107
[14] Vanderbilt D and Resta R 2006 Conceptual foundations of materials: A standard model for ground- and
excited-state properties ed S G Louie and M L Cohen (Amsterdam: Elsevier) p 139
[15] Resta R and Vanderbilt D 2007 Physics of Ferroelectrics: a Modern Perspective (Topics in Applied Physics
vol 105) ed Ch H Ahn, K M Rabe and J-M Triscone (Berlin: Springer) p 31
[16] Souza I, Iñiguez J and Vanderbilt D 2002 Phys. Rev. Lett. 89 117602
[17] Umari P and Pasquarello A 2002 Phys. Rev. Lett. 89 157602
[18] Sai N, Rabe K M and Vanderbilt D 2002 Phys. Rev. B 66 104108
[19] Car R and Parrinello M 1985 Phys. Rev. Lett. 55, 2471; Remler D K and Madden P 1990 Mol. Phys. 70 921;
Galli G and Pasquarello A 1993 Computer Simulations in Chemical Physics ed M Allan and D Tildesley
(Dordrecht: Kluwer) p 261
[20] Debernardi A, Bernasconi M, Cardona M and Parrinello M 1997 Appl. Phys. Lett. 71 2692; Sivestrelli P L,
Bernasconi M and Parrinello M 1997 Chem. Phys. Lett. 277 478; Pasquarello A and Car R, Phys. Rev.
Lett. 79 1766; Bernasconi M, Sivestrelli P L and Parrinello M 1998 Phys. Rev. Lett. 81 1235
[21] Resta R, Pusternak M and Baldereschi A 1993 Phys. Rev. Lett. 70 1010
[22] Dall’Olio S, Dovesi R and Resta R 1997 Phys. Rev. B 56 10105
[23] Ch H Ahn, K M Rabe and J-M Triscone 2007 Physics of Ferroelectrics: a Modern Perspective (Topics in
Applied Physics vol 105) (Berlin: Springer)