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Theory of polarization of crystalline solids

R. D. King-Smith and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, P. O. Box 849, Piscataway, New Jersey 08855-0849
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We consider the change in polarization $\Delta\mathbf{P}$ which occurs upon making an adiabatic change in the Kohn-Sham Hamiltonian of the solid. A simple expression for $\Delta\mathbf{P}$ is derived in terms of the valence-band wave functions of the initial and final Hamiltonians. We show that physically $\Delta\mathbf{P}$ can be interpreted as a displacement of the center of charge of the Wannier functions. The formulation is successfully applied to compute the piezoelectric tensor of GaAs in a first-principles pseudopotential calculation.

Experimentally changes in the electrical polarization of solids can be induced by various means including application of a strain (piezoelectricity) or changes in temperature (pyroelectricity). Ferroelectrics are a technologically important class of materials whose polarization can be switched by application of an electric field.[1] To date there have been relatively few theoretical attempts to calculate these quantities from a quantum-mechanical starting point. In this paper we derive simple formulas for calculating finite changes in the polarization of a crystalline solid. The method is ideally suited to first-principles density-functional investigations of polarization effects.

We begin by considering the change in the electronic polarization per unit volume of a crystal which is induced upon making an adiabatic change in the self-consistent Kohn-Sham potential. We parametrize the change in the potential with a variable λ which is arranged to have values 0 and 1 at initial and final values of the potential, respectively. In the following we shall specialize to the case where the change in potential preserves the translational symmetry of the solid. The formalism developed below will therefore be applicable for computing $\Delta\mathbf{P}$ with macroscopic electric field $\mathbf{E}$ held to be zero. If the material is an insulator for all values of λ in the range 0–1 then we have

$$\partial P_\alpha/\partial\lambda=-\frac{ifq_e\hbar}{N\Omega m_e}\sum_{\mathbf{k}}\sum_{n=1}^{M}\sum_{m=M+1}^{\infty}\frac{\langle\psi_{\mathbf{k}n}^{(\lambda)}|\hat{p}_\alpha|\psi_{\mathbf{k}m}^{(\lambda)}\rangle\langle\psi_{\mathbf{k}m}^{(\lambda)}|\partial V_{\mathrm{KS}}^{(\lambda)}/\partial\lambda|\psi_{\mathbf{k}n}^{(\lambda)}\rangle}{(\epsilon_{\mathbf{k}n}^{(\lambda)}-\epsilon_{\mathbf{k}m}^{(\lambda)})^2}+\text{c.c.}\ , \tag{1}$$

where α is a Cartesian direction, m_e and q_e are the electron mass and charge, N is the number of unit cells in the crystal, Ω is the volume of a unit cell, f is the occupation number of states in the valence band (in spin-degenerate systems $f=2$), M is the number of occupied bands, $\hat{p}$ is the momentum operator, and $V_{\mathrm{KS}}^{(\lambda)}$ is the Kohn-Sham potential. A heuristic derivation of Eq. (1) has recently been given by Resta.[2] Resta proposes that we compute the total change in polarization per unit volume, $\Delta\mathbf{P}$, using

$$\Delta\mathbf{P}=\int_0^1(\partial\mathbf{P}/\partial\lambda)d\lambda\ . \tag{2}$$

Physically, $\Delta\mathbf{P}$ arises from the flow of polarization currents in the solid and Eq. (1) may also be regarded as the adiabatic limit of a Kubo formula for the current.[3] It is somewhat surprising that the change in polarization can be computed without explicitly stating how the crystal is terminated. The fundamental justification for taking the thermodynamic limit in Eq. (1) rests with the fact that the current response of an insulator depends only on the local environment.[4,5]

The expression for $\partial\mathbf{P}/\partial\lambda$ can be recast in a form in which conduction-band states do not explicitly appear using an argument developed by Thouless *et al.*[6] in their analysis of the quantum Hall effect. We introduce a set of cell-periodic functions, $u_{\mathbf{k}n}^{(\lambda)}$, with a choice of phases such that $u_{\mathbf{k}n}^{(\lambda)}$ are analytic in both $\mathbf{k}$ and λ. The matrix elements in Eq. (1) can be rewritten as

$$\langle\psi_{\mathbf{k}n}^{(\lambda)}|\hat{p}_\alpha|\psi_{\mathbf{k}m}^{(\lambda)}\rangle=\frac{m_e}{\hbar}\langle u_{\mathbf{k}n}^{(\lambda)}|[\partial/\partial k_\alpha,\hat{H}_{\mathbf{k}}^{(\lambda)}]|u_{\mathbf{k}m}^{(\lambda)}\rangle \tag{3a}$$

and

$$\langle\psi_{\mathbf{k}n}^{(\lambda)}|\partial V_{\mathrm{KS}}^{(\lambda)}/\partial\lambda|\psi_{\mathbf{k}m}^{(\lambda)}\rangle=\langle u_{\mathbf{k}n}^{(\lambda)}|[\partial/\partial\lambda,\hat{H}_{\mathbf{k}}^{(\lambda)}]|u_{\mathbf{k}m}^{(\lambda)}\rangle\ , \tag{3b}$$

where the $\hat{H}_{\mathbf{k}}^{(\lambda)}$ is the cell-periodic Hamiltonian

$$\hat{H}_{\mathbf{k}}^{(\lambda)}=(1/2m_e)(-i\hbar\nabla+\hbar\mathbf{k})^2+V_{\mathrm{KS}}^{(\lambda)}(r)\ . \tag{3c}$$

Substituting Eqs. (3a) and (3b) into Eq. (1) it is straightforward to show by analogy with Ref. 6 that

$$\Delta P_\alpha=-(ifq_e/8\pi^3)\sum_{n=1}^{M}\int_{\mathrm{BZ}}d\mathbf{k}\int_0^1 d\lambda[\langle\partial u_{\mathbf{k}n}^{(\lambda)}/\partial k_\alpha|\partial u_{\mathbf{k}n}^{(\lambda)}/\partial\lambda\rangle-\langle\partial u_{\mathbf{k}n}^{(\lambda)}/\partial\lambda|\partial u_{\mathbf{k}n}^{(\lambda)}/\partial k_\alpha\rangle]\ , \tag{4}$$

where the integral over $\mathbf{k}$ extends over any primitive cell in reciprocal space. The one-dimensional (1D) analogue of Eq. (4) has been derived previously by Thouless[7] in a slightly different context for the case of noninteracting electrons where the formal similarities with the quantum Hall effect are particularly striking. For example, in a

1D system with period a, Stokes's theorem allows us to write the change in polarization per unit length as

$$\Delta P=-\frac{fq_e}{2\pi}\sum_{n=1}^{M}\left\{i\oint_C\sum_{j=1}^{2}d\tau_j\langle u_{\mathbf{k}n}^{(\lambda)}|\partial/\partial\tau_j|u_{\mathbf{k}n}^{(\lambda)}\rangle\right\}, \tag{5}$$

where τ is a two-component vector with elements (λ,k) and the contour of integration C is around the loop in τ space from $(0,\pi/a)\rightarrow(1,\pi/a)\rightarrow(1,-\pi/a)\rightarrow(0,-\pi/a)\rightarrow(0,\pi/a)$. The quantity in curly brackets can be recognized as the change in Berry phase for fictitious adiabatic evolution of the cell-periodic wave function around the loop C.[8,9] Thouless has observed that the contour integral in Eq. (5) is quantized in the special case where the potential is the same at $\lambda=1$ and 0. In these circumstances the quantity in curly brackets measures the change in the phase of the wave function at any given real-space point as (λ,k) is taken around C. Given that the cell-periodic parts of the wave function can be chosen to be analytic in k and λ this change in phase must be an integer multiple of 2π. We therefore conclude that the polarization per unit length of a 1D system can only change by an integer multiple of fe for adiabatic changes in the Hamiltonian for which $V_{\mathrm{KS}}^{(0)}=V_{\mathrm{KS}}^{(1)}$. An analogous result for 3D systems will be derived below.

The physical content of Eq. (4) can be made more readily apparent by working in a gauge where the wave functions are periodic in reciprocal space, i.e., $\psi_{\mathbf{k},n}^{(\lambda)}(\mathbf{r})=\psi_{\mathbf{k}+\mathbf{G},n}^{(\lambda)}(\mathbf{r})$ for all reciprocal lattice vectors $\mathbf{G}$. In terms of the cell-periodic functions in such a gauge we have

$$u_{\mathbf{k},n}^{(\lambda)}(\mathbf{r})=e^{i\mathbf{G}\cdot\mathbf{r}}u_{\mathbf{k}+\mathbf{G},n}^{(\lambda)}(\mathbf{r}) . \tag{6}$$

We remark that the gauge condition of Eq. (6) does not uniquely define the phase of the wave functions. Integrating Eq. (4) by parts we find that

$$\Delta P_\alpha=\frac{ifq_e}{8\pi^3}\sum_{n=1}^{M}\int_{\mathrm{BZ}}d\mathbf{k}\left\{[\langle u_{\mathbf{k}n}^{(\lambda)}|\partial/\partial k_\alpha|u_{\mathbf{k}n}^{(\lambda)}\rangle]_0^1-\int_0^1 d\lambda\frac{\partial}{\partial k_\alpha}\langle u_{\mathbf{k}n}^{(\lambda)}|\partial/\partial\lambda|u_{\mathbf{k}n}^{(\lambda)}\rangle\right\} . \tag{7}$$

With our choice of gauge, $\langle u_{\mathbf{k}n}^{(\lambda)}|\partial/\partial\lambda|u_{\mathbf{k}n}^{(\lambda)}\rangle$ is periodic in $\mathbf{k}$. The gradient of this quantity integrated over the Brillouin zone (BZ) is therefore zero, so the second term in Eq. (7) makes no contribution. In the periodic gauge we therefore arrive at the conclusion that

$$\Delta\mathbf{P}=\mathbf{P}^{(1)}-\mathbf{P}^{(0)} , \tag{8a}$$

where

$$P_\alpha^{(\lambda)}=(ifq_e/8\pi^3)\sum_{n=1}^{M}\int_{\mathrm{BZ}}d\mathbf{k}\langle u_{\mathbf{k}n}^{(\lambda)}|\partial/\partial k_\alpha|u_{\mathbf{k}n}^{(\lambda)}\rangle . \tag{8b}$$

The integral on the right-hand side of Eq. (8b) is closely related to the Berry phase of band n, a quantity which has been recently introduced by Zak and co-workers.[10] The form of Eq. (8) is particularly simple when written in terms of the Wannier functions $W_n^{(\lambda)}(\mathbf{r})$ of the occupied bands.[10] The Wannier functions depend on the particular choice of phases used in the periodic gauge. We define the Wannier function using

$$W_n^{(\lambda)}(\mathbf{r}-\mathbf{R})=(\sqrt{N}\,\Omega/8\pi^3)\int_{\mathrm{BZ}}d\mathbf{k}\,e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}u_{\mathbf{k}n}^{(\lambda)}(\mathbf{r}) \tag{9a}$$

which implies that

$$u_{\mathbf{k}n}^{(\lambda)}(\mathbf{r})=(1/\sqrt{N})\sum_{\mathbf{R}}e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}W_n^{(\lambda)}(\mathbf{r}-\mathbf{R}) , \tag{9b}$$

where the sum over $\mathbf{R}$ runs over all real-space lattice vectors. Substituting Eq. (9b) into (8b) we find the simple result that

$$\mathbf{P}^{(\lambda)}=(fq_e/\Omega)\sum_{n=1}^{M}\int\mathbf{r}|W_n^{(\lambda)}(\mathbf{r})|^2d\mathbf{r} . \tag{10}$$

Physically, Eqs. (8a) and (10) state that the change in polarization of the solid is proportional to the displacement of the center of charge of the Wannier functions induced by the adiabatic change in the Hamiltonian.

Returning to the case where the Hamiltonians at $\lambda=0$ and 1 are identical, $u_{\mathbf{k}n}^{(0)}(\mathbf{r})$ and $u_{\mathbf{k}n}^{(1)}(\mathbf{r})$ can at most differ by a phase factor so that

$$u_{\mathbf{k}n}^{(1)}(\mathbf{r})=e^{i\theta_{\mathbf{k}n}}u_{\mathbf{k}n}^{(0)}(\mathbf{r}) . \tag{11}$$

In this limit Eq. (8) reduces to

$$\Delta P_\alpha=-(fq_e/8\pi^3)\sum_{n=1}^{M}\int_{\mathrm{BZ}}d\mathbf{k}\,\partial\theta_{\mathbf{k}n}/\partial k_\alpha . \tag{12}$$

With our periodic choice of gauge $e^{i\theta_{\mathbf{k}n}}$ must be periodic in $\mathbf{k}$. The most general form for the phase angle under these circumstances is $\theta_{\mathbf{k}n}=\beta_{\mathbf{k}n}+\mathbf{k}\cdot\mathbf{R}_n$, where $\beta_{\mathbf{k}n}$ is periodic in $\mathbf{k}$. We thus conclude that

$$\Delta\mathbf{P}=(fq_e/\Omega)\sum_{n=1}^{M}\mathbf{R}_n . \tag{13}$$

The change in polarization per unit volume for paths where the Hamiltonian returns to itself is therefore quantized in units of $(fq_e/\Omega)\mathbf{R}$. A particularly simple case to consider is the magnitude of $\Delta\mathbf{P}$ for paths of the form $V_{\mathrm{KS}}^{(\lambda)}(\mathbf{r})=V_{\mathrm{KS}}^{(0)}(\mathbf{r}-\lambda\mathbf{R})$, which physically corresponds to a translation of the crystal. In this case it is straightforward to verify by explicit calculation that Eq. (8) yields $\Delta\mathbf{P}=(fq_e/\Omega)M\mathbf{R}$, as one would expect on physical grounds.

We have in Eqs. (8) and (13) the rather remarkable result that $\Delta\mathbf{P}$ for a crystal can in principle be determined, to within a factor of $(fe/\Omega)\mathbf{R}$, from a knowledge of the valence-band Kohn-Sham wave functions at $\lambda=0$ and 1. In practice the arbitrary factor of $(fe/\Omega)\mathbf{R}$ can often be eliminated by inspection because one is usually interested in polarization changes where $|\Delta\mathbf{P}|\ll|(fe/\Omega)\mathbf{R}_1|$ where $\mathbf{R}_1$ is the shortest nonzero real-space lattice vector. In

other cases any uncertainties introduced by this factor can always be removed by dividing the change in the Hamiltonian into a number of subintervals.

Direct evaluation of $\Delta\mathbf{P}$ via Eq. (8) is cumbersome in numerical calculations, because in practice we only compute the wave functions at a finite number of points in the Brillouin zone, and in general there will be no particular phase relationship between the eigenvectors generated by the diagonalization routine. In actual calculations we circumvent this difficulty using the following strategy. First we pick a direction parallel to a short reciprocal-lattice vector of the solid, $\mathbf{G}_\parallel$. We choose the primitive cell for the $\mathbf{k}$-space integration to be a prism with its axis aligned along $\mathbf{G}_\parallel$. The component of $\Delta\mathbf{P}$ directed along $\mathbf{G}_\parallel$ can be written

$$\Delta P_\parallel = P_\parallel^{(1)} - P_\parallel^{(0)} , \tag{14a}$$

where, in an obvious notation

$$P_\parallel^{(\lambda)} = \frac{ifq_e}{8\pi^3} \int_A d\mathbf{k}_\perp \sum_{n=1}^{M} \int_0^{|\mathbf{G}_\parallel|} dk_\parallel \left\langle u_{\mathbf{k}n}^{(\lambda)} \left| \frac{\partial}{\partial k_\parallel} \right| u_{\mathbf{k}n}^{(\lambda)} \right\rangle . \tag{14b}$$

The integration in the perpendicular direction poses no special problems and can be performed by sampling over a 2D mesh of k points generated, for example, using the Monkhorst-Pack method.[12] To perform the integral over $k_\parallel$ at each point in the $k_\perp$ mesh we compute the cell-periodic parts of the wave functions at the string of J k points at $\mathbf{k}_j = \mathbf{k}_\perp + j\mathbf{G}_\parallel/J$ where j runs from 0 to $J-1$. We then compute the variable $\phi_J^{(\lambda)}(\mathbf{k}_\perp)$ defined through

$$\phi_J^{(\lambda)}(\mathbf{k}_\perp) = \mathrm{Im}\left\{ \ln \prod_{j=0}^{J-1} \det(\langle u_{\mathbf{k}_j,m}^{(\lambda)} | u_{\mathbf{k}_{j+1},n}^{(\lambda)} \rangle) \right\} , \tag{15}$$

where it is understood that $u_{\mathbf{k}_J,n}^{(\lambda)} = e^{-i\mathbf{G}_\parallel\cdot\mathbf{r}} u_{\mathbf{k}_0,n}^{(\lambda)}$. The determinant in Eq. (15) is that of the $M\times M$ matrix formed by allowing n and m to run over all valence bands. With an analytic choice of cell-periodic wave functions it can be verified that

$$\begin{aligned} \phi^{(\lambda)}(\mathbf{k}_\perp) &\equiv \lim_{J\to\infty} \phi_J^{(\lambda)}(\mathbf{k}_\perp) \\ &= -i \sum_{n=1}^{M} \int_0^{|\mathbf{G}_\parallel|} dk_\parallel \langle u_{\mathbf{k}n}^{(\lambda)} | \partial/\partial k_\parallel | u_{\mathbf{k}n}^{(\lambda)} \rangle \end{aligned} \tag{16a}$$

so our expression for $P_\parallel^{(\lambda)}$ becomes

$$P_\parallel^{(\lambda)} = -(fq_e/8\pi^3) \int_A d\mathbf{k}_\perp \phi^{(\lambda)}(\mathbf{k}_\perp) . \tag{16b}$$

It is straightforward to confirm that the product over j in Eq. (15) is independent of how the phases of the wave functions are chosen. Changes of the phase of $u_{\mathbf{k}n}^{(\lambda)}$ can change the value of the integral in Eq. (16) by an integer multiple of 2π. Correspondingly the arbitrary constant in the definition of $\phi_J^{(\lambda)}(\mathbf{k}_\perp)$ given in Eq. (15) arises from the fact that the imaginary part of the log of a complex number is only defined up to a constant multiple of 2π. In practice the arbitrary constant is removed by comparing $\phi_J^{(1)}(\mathbf{k}_\perp)$ with $\phi_J^{(0)}(\mathbf{k}_\perp)$ using the argument outlined in the previous paragraph.

We have in Eqs. (14)–(16) all the ingredients necessary for computing polarization changes in a practical calculation. Within this approach the need for supercells or linear-response techniques is completely avoided.[11] The method is ideally suited to modern electronic structure methods based on iterative diagonalization techniques, which concentrate on computing the valence-band wave functions only.[13]

We illustrate the approach by computing the transverse effective charge tensor and piezoelectric constant of GaAs in a first-principles pseudopotential calculation. The effective charge of GaAs may be determined by computing the change in polarization which is induced on making a small displacement of one sublattice with the boundary condition $\mathbf{E}=\mathbf{0}$. For example, if we move the Ga sublattice by a vector $\mathbf{u}$, then the electronic contribution to the polarization difference between the distorted and undistorted structures is

$$\Delta\mathbf{P} = (e/\Omega) Z_{\mathrm{Ga}}^{*(\mathrm{el})} \mathbf{u} , \tag{17}$$

where $Z_{\mathrm{Ga}}^{*(\mathrm{el})}$ is the electronic contribution to the effective charge. The piezoelectric tensor γ is the strain derivative of the polarization under boundary conditions of $\mathbf{E}=\mathbf{0}$.[4] In the zinc-blende structure there is only one independent component of the piezoelectric tensor, γ_{14}. The piezoelectric tensor can be thought of as the sum of two independent terms. The first term, which we denote by $\gamma_{14}^{(0)}$ following Ref. 11, arises from the change in polarization when the ions are subjected to a homogeneous strain. The second contribution owes its origin to the relative displacement of the sublattices, and can be expressed in terms of the effective charges and internal strain parameters.[4,11] It is shown in Ref. 11 that

$$(a^2/e)\gamma_{14} \equiv \bar{\gamma}_{14} = (a^2/e)\gamma_{14}^{(0)} + Z_{\mathrm{Ga}}^{*}\xi , \tag{18}$$

where ξ is the internal strain parameter.

Our first-principles calculations used norm-conserving nonlocal pseudopotentials.[14] We note in passing that, strictly speaking, a nonlocal potential causes a modification to the momentum operator in Eq. (1).[2] However, in this situation there is a precisely compensating change to the Hamiltonian for the cell-periodic part of the wave function, and equations from Eq. (4) on remain correct at they stand. Our calculation treated exchange and correlation in the local-density approximation using the Wigner form. The wave functions were expanded using a 20-Ry plane-wave cutoff. All calculations of the self-consistent Kohn-Sham potential were performed with a (4,4,4) Monkhorst-Pack mesh.[12] Calculations in the cubic structure were performed at the theoretical lattice constant a, which came out to be 5.576 Å with the above parameters. For the calculations of the effective charge we displaced the Ga atom a distance of $0.01a$ in the (001) direction and computed the polarization change in the z direction. The integration mesh for computing $\Delta\mathbf{P}$ used 16 k points in the $\mathbf{k}_\perp$ mesh and a string of 10 k points in the parallel direction. We obtained $\gamma_{14}^{(0)}$ by computing the change in polarization in the z directions induced by applying a 1% xy shear strain to the crystal.

The results of our calculation are summarized in Table

I. The total value of Z^*_{Ga} (electronic plus ionic contributions) came out to be 1.984, in excellent agreement with the value of 1.994 obtained from pseudopotential linear-response calculations.[11] Both sets of theoretical values of Z^*_{Ga} are about 8% smaller than the experimental value. Our calculations on the strained crystal yielded a $(a^2/e)\gamma^{(0)}_{14}$ of -1.352. The value agrees to better than 5% with the result obtained from linear-response methods.[11] Our overall value for the piezoelectric constant $\bar{\gamma}_{14}$ was -0.28, compared with an experimental value of -0.32. The agreement between our calculation and experiment is reasonable, given that the two terms in Eq. (18) show a strong tendency to cancel. We have checked that our calculation is converged with respect to k-point set and plane-wave cutoff, and that the polarization response is linear in the applied perturbation. We attribute the small differences between our results and those of Gironcoli, Baroni, and Resta[11] to the use of different pseudopotentials and parametrizations of the exchange and correlation potential.

Before closing we note that it is tempting to physically identify the quantity $\mathbf{P}^{(\lambda)}$ defined in Eq. (8b) as the absolute polarization of the perturbed crystal. Of course it would have to be understood that the polarization, defined in this way, would only be well defined modulo $ef\mathbf{R}/\Omega$. The conditions under which such an identification is useful will be the subject of a future communication.

TABLE I. Theoretical and experimental piezoelectric response of GaAs.

	This work	Linear response[a]	Experiment
a (Å)	5.576	5.496	5.642
ξ	0.542	0.528	0.55
Z^*_{Ga}	1.984	1.994	2.16
$(a^2/e)\gamma^{(0)}_{14}$	-1.352	-1.405	
$\bar{\gamma}_{14}$	-0.28	-0.35	-0.32

[a]Reference 11.

In conclusion, we have shown that adiabatic changes in the Kohn-Sham Hamiltonian lead to polarization changes in the solid which can be computed in terms of the initial and final valence-band wave functions of the system. This result forms the basis for a scheme for computing polarization changes of solids within the context of first-principles total-energy calculations.

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