PHYSICAL REVIEW B VOLUME 58, NUMBER 23 15 DECEMBER 1998-I

Electronic dielectric constants of insulators calculated by the polarization method

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(Received 4 June 1998)

We discuss a nonperturbative, technically straightforward, easy-to-use, and computationally affordable method, based on polarization theory, for the calculation of the electronic dielectric constant of insulating solids at the first-principles level. We apply the method to GaAs, AlAs, InN, SiC, ZnO, GaN, AlN, BeO, LiF, $PbTiO_3$, and $CaTiO_3$. The predicted ε^{∞}'s agree well with those given by density-functional perturbation theory (the reference theoretical treatment), and they are generally within less than 10% of experiment. [S0163-1829(98)09739-6]

The electronic dielectric constant ε^{∞}, measuring the response to a uniform electrostatic field, is a fundamental quantity in basic and applied solid-state physics. Besides its intrinsic interest, knowledge of ε^{∞} is crucial to a calculation of the static dielectric constant ε^{0}. *Ab initio* calculations of ε^{∞} have been performed in recent times by density-functional perturbation theory (DFPT) (Refs. 1–3) for a host of different materials. Here we discuss a method to compute ε^{∞} based on density-functional theory[4] and the modern theory of dielectric polarization,[5] and apply it to a set of polar crystals. Despite its simplicity and ease of use, the method predicts ε^{∞}'s in close agreement with those obtained by DFPT. This suggests that theoretical predictions deviate from (and typically overestimate) the experimental value on account of density-functional theory, and not of the specific method or implementation.

We have sketched the basics of the method in a report on the calculation of the static dielectric constant.[6] Almost all the ingredients needed to evaluate the latter can be obtained from *ab initio* calculations of total energy, stress, forces, and dielectric polarization in zero field (by the Berry-phase approach[5,7]) for bulk systems. The notable exception is the electronic dielectric constant ε^{∞}, for which we follow the alternate approach described below.

Theory. The core of the argument is that ε^{∞} can be obtained from the relationship between macroscopic polarization in zero field and interface charge accumulation[6,8,9] in appropriate superlattices. An insulating superlattice is constructed, which consists of periodically alternating slabs of equal length, stacked along some fixed direction and made of materials 1 and 2. In such a superlattice, in the absence of external sources of fields, the displacement field orthogonal to the interfaces is conserved:

$$D_1 = E_1 + 4\pi P_1(E_1) = E_2 + 4\pi P_2(E_2) = D_2. \qquad (1)$$

We expand the polarization to first order in the screened fields in the two materials, indexed by i:

$$P_i(E) = P_i^{(0)} + \chi_i E_i, \qquad (2)$$

where P_i^0 is the *zero-field* polarization, and χ_i the susceptibility of material i. The presence of a zero-field polarization is important: substituting the last relation into Eq. (1), one obtains

$$4\pi(P_2^{(0)} - P_1^{(0)}) = \varepsilon_1^{\infty} E_1 - \varepsilon_2^{\infty} E_2. \qquad (3)$$

(In this context, it does not matter whether the zero-field polarization is spontaneous or piezoelectric, or a combination of the two.) Only for a null P_i^0 does one recover the familiar equality

$$\varepsilon_1^{\infty} E_1 = \varepsilon_2^{\infty} E_2. \qquad (4)$$

To proceed further, one notes that periodic boundary conditions imply

$$E \equiv E_1 = -E_2, \quad \Delta E \equiv E_1 - E_2 = 2E,$$

and therefore Eq. (3) becomes

$$4\pi(P_2^{(0)} - P_1^{(0)}) = \tfrac{1}{2}(\varepsilon_1^{\infty} + \varepsilon_2^{\infty})\Delta E. \qquad (5)$$

Recalling that the charge accumulation per unit area at the interface between materials 1 and 2 is $s_{\mathrm{int}} = \pm \Delta E / 4\pi$, we finally obtain

$$s_{\mathrm{int}} = \pm 2(P_2^{(0)} - P_1^{(0)})/(\varepsilon_1^{\infty} + \varepsilon_2^{\infty}) = \pm 2\Delta P^{(0)}/(\varepsilon_1^{\infty} + \varepsilon_2^{\infty}). \qquad (6)$$

This relation connects the *difference* in macroscopic bulk polarization at zero field with the components $\varepsilon_{1,2}^{\infty}$ of the dielectric tensors of the interfaced materials along the interface normal.[10]

In an undistorted homojunction, i.e., a superlattice in which material 1 is identical to material 2, there is effectively no interface. Therefore, there is no polarization change, and the interface charge is zero. It is nevertheless possible to generate a polarization difference in a controlled manner, by inducing a small distortion δ of one of the atomic sublattices in half of the superlattice unit cell. This produces a difference in polarization, and a charge accumulation at the interface. The interface charge s_{int} at the interface between distorted and undistorted regions can be easily calculated via macroscopic averaging[8,11] of the charge density. On the other hand, the zero-field polarizations $\mathbf{P}_2$ for the bulk material in

TABLE I. Theoretical structural parameters for the materials being studied.

	Structure	a_0 (bohr)	c_0/a_0	u_0
GaAs	zinc blende	10.60		
AlAs	zinc blende	10.62		
LiF	rocksalt	7.50		
AlN	wurtzite	5.82	1.619	0.380
GaN	wurtzite	6.04	1.634	0.376
InN	wurtzite	6.66	1.627	0.377
BeO	wurtzite	5.00	1.610	0.377
ZnO	wurtzite	5.98	1.616	0.376
$PbTiO_3$	cubic	7.34		
$CaTiO_3$	cubic	7.20		

the undistorted state, and $\mathbf{P}_1$ for the bulk material in the same strain state as in the superlattice, are evaluated using the Berry-phase technique. From Eq. (6), one then extracts the average electronic dielectric constant $\overline{\varepsilon}^{\infty}=(\varepsilon_1^{\infty}+\varepsilon_2^{\infty})/2$.

By construction ε_2 equals the dielectric constant, while ε_1, the dielectric constant in the distorted state, of course does not. Therefore $\overline{\varepsilon}$ does not equal the sought-after dielectric constant for $\delta\neq 0$. However, $\overline{\varepsilon}$ does equals the dielectric constant (the tensor component along $\hat{\mathbf{n}}$) in the limit of zero distortion:

$$\varepsilon^{\infty}=\lim_{\delta\to 0}\overline{\varepsilon}.$$

This limit can be evaluated with essentially arbitrary accuracy by extrapolation or interpolation. Also, since the materials involved in the heterojunction are identical modulo a vanishingly small distortion, it is virtually guaranteed that no interface state exists, so that no band bending or electrostatic perturbation adulterates the polarization effects.

Summarizing, in the present approach the dielectric constant is simply obtained using the geometric quantum phase polarization and relatively small, accurately controllable supercell calculations. In the latter calculations, the slabs should be short enough that the constant electric field will not cause metallization, and the slabs should be sufficiently long to recover bulklike behavior away from the interfaces. Both requirements are generally also met by materials with small calculated gaps if sufficiently small strains are applied. Unlike DFPT, the present method does not resort to perturbation theory, and it is interesting in that the determination of the electronic screening uses the connection with the geometric quantum phase.[12] The calculations involved are nonintensive, and can be performed even on Pentium-like personal computers. Also, since the implementation is very much simpler than that of DFPT, the method seems promising as a general-purpose tool for nonspecialists.

Applications. We now apply the method to a set of representative polar materials of general interest: SiC, GaAs, AlAs, InN, GaN, AlN, BeO, ZnO, LiF, cubic $PbTiO_3$, and cubic $CaTiO_3$. All our calculations, as detailed below, are done in the local-density approximation to density-functional theory.[4] Our results are compared to results of DFPT calculations (where available), which effectively function as reference for computational methods in this area. Comparison with experiment is also presented when possible.

TABLE II. Electronic dielectric constants of several polar insulators. Our calculated values are compared with theoretical DFPT values and with experiment.

	Present	DFPT	Expt.
GaAs	12.53	12.3 [a]	10.9 [b]
AlAs	9.37	9.2 [a]	8.2 [b]
InN	8.49		8.40 [b]
w-SiC	7.07	7.28 [c]	6.65 [c]
GaN	5.69	5.41 [d]	5.70 [e]
ZnO	4.65		4.60 [b]
AlN	4.61	4.62 [f]	4.68 [g]
BeO	3.15		2.99 [h]
LiF	2.19		1.96 [b]
$PbTiO_3$	8.28	8.24 [i]	8.64 [j]
$CaTiO_3$	5.87		5.81 [j]

[a] Reference 2.
[b] Reference 20.
[c] Reference 17.
[d] Reference 18.
[e] Reference 21.
[f] Reference 19.
[g] Reference 22.
[h] Reference 23.
[i] Reference 3.
[j] Reference 24.

In the calculations we use the Ceperley-Alder exchange-correlation energy[13] and ultrasoft pseudopotentials[14] for the electron-ion interaction. The pseudopotentials have been constructed to include the following semicore states in the valence manifold: Zn and Ga $3d$, In $4d$; Li $1s$; Pb $5d$, Ti and Ca $3s3p$. A plane-wave basis with 25-Ry cutoff is found to be sufficient to converge the quantities of interest in all the materials investigated. Bulk Brillouin-zone summations are done over appropriate Chadi-Cohen[15] k-point meshes for the relevant structures. Bulk polarizations are obtained in all cases via the Berry-phase technique[5,7] using a 16-point Monkhorst-Pack[16] k-point mesh in the a-plane direction, and a ten-point uniform mesh in the c direction. For the supercell calculation, we have employed superlattices including typically 16–20 atoms, oriented along (0001) for wurtzites, (111) or (100) for zinc blende, (100) for the NaCl structure, and (100) for cubic perovskites. (Note that wurtzite has two independent components of the dielectric tensor, and the one we are actually calculating is that along the polar axis.) In the supercell calculations, downfolded meshes were used comprising 12 k points for wurtzite and zinc blende, eight points for the NaCl structure, and 12 points for perovskites. The cation sublattice displacements δ are typically 0.05–0.1% of the bond length. Ionic relaxation is never allowed, so that the response is purely electronic. All the calculations are performed at the theoretical lattice constants, that are reported in Table I.

With the above reported theoretical ingredients, we obtained the theoretical values of ε^{∞} listed in Table II together with DFPT and experimental values, and plotted in Fig. 1 versus the experimental values for the different materials.

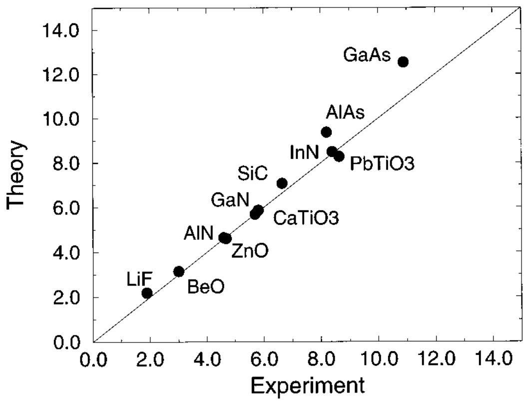

FIG. 1. Present theoretical ε^∞ vs experimental values.

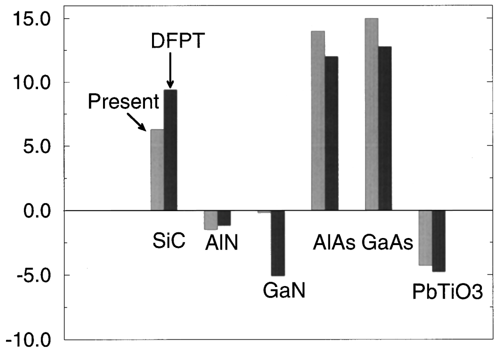

FIG. 2. Relative percental error in ε^∞ for DFPT and the present method (see text).

The general level of agreement seems quite good on the scale of Fig. 1. To give a closer view, in Fig. 2 we display the relative percental deviation of the theoretical ε^∞ with respect to experiment, both for our method and DFPT.

Discussion. The main content of Fig. 2 is that DFPT and the present method agree quite closely (the deviation for GaN is probably due to a different treatment of the Ga $3d$ electrons). It thus appears that deviations from experiment are not related to the specific method used, but are likely to be a token of the underlying density functional formalism. Most theoretical values are overestimates of the experimental data, the main exception being the 4% underestimate for $\mathrm{PbTiO_3}$, both in DFPT (Ref. 3) (at the experimental lattice constant) and in the present method (at the theoretical lattice constant). This is possibly due to the uncertainties in the experimental values, which are in fact plasmon-pole extrapolations[24] to optical $\omega=0$ of values measured in the visible at relatively high temperature, while the calculation is at zero temperature and zero ω (in fact, this holds also for $\mathrm{CaTiO_3}$). Indeed, the situation for perovskites (even in the paraelectric phase) is far from settled in general; other recent linear response results of another group[25,26] overestimate experiment considerably: the ε^∞ reported for cubic $\mathrm{SrTiO_3}$ is 6.63 compared with 4.69 experimental,[25] and also 6.63 compared with 5.18 experimental for cubic $\mathrm{KNbO_3}$.[26]

It should be mentioned that ε^∞ in our scheme is actually a finite-q value due to the finiteness of the simulation supercell, and this may cause some additional deviation as compared to DFPT. However, in our supercells the minimum q is quite small (~ 0.03 bohr^{-1}), and inspection of the typical structure[27] of ε^∞ as a function of q reveals that the deviations to be expected are in the order of 1%.

In closing, we discuss the case of nonpolar materials: in such a case, the procedure outlined above does not apply, since no macroscopic polarization can occur in a system containing only a nonpolar material. However, since the internal fields in the superlattice layers are *proportional to* ΔP, we can set up a superlattice by alternating layers of the unpolarized material of interest and layers of some appropriate polarized material. The latter effectively function as a polarization supply for the unpolarized layer. In practice, to compute the dielectric constant of Si, we first calculate the dielectric constant and zero-field polarization for some polarized material, say SiC, in the wurtzite structure. We then stack along the (111) direction of zinc blende [i.e. (0001) of wurtzite], a superlattice such as [.../SiC/Si/SiC/Si/...]. Since SiC is polarized and we use periodic boundary conditions, the interface charge is

$$s_{\mathrm{int}}=\pm 2P^{(0)}_{\mathrm{SiC}}/(\varepsilon^{\infty}_{\mathrm{SiC}}+\varepsilon^{\infty}_{\mathrm{Si}}), \tag{7}$$

from which the dielectric constant of Si is trivially extracted. SiC should have the in-plane lattice constant of Si in order to avoid strain effects in the Si layer. Clearly its calculated properties in this specific, hypothetical realization are irrelevant: what counts is that it provides the polarization to create an interface charge and a depolarizing field inside Si. The above scheme, it turns out, is more of conceptual interest than of practical use for nonpolar solids: interface states occur fairly easily at heterovalent junctions, spoiling the applicability of Eq. (7). Applying the scheme in practice to nonpolar solids will require quite some trial and error to identify a ''clean'' interface, and we did not pursue this further here.

Summary. In conclusion, our results indicate that the polarization-based method can produce theoretical dielectric constants within $\sim 5-10\,\%$ of experiment, and is as accurate as DFPT. While much more limited in its general scope, our method appears to be a useful alternative to DFPT for this kind of calculations.

We thank Elena Manca for help in the perovskite calculations, and acknowledge special support from INFM within the PAISS program.

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$$\Delta \mathbf{P_e} = -\frac{2e}{(2\pi)^3}\int_{\lambda_1}^{\lambda_2} d\lambda \int_{BZ} d\mathbf{k}\,\frac{\partial^2}{\partial\lambda\,\partial\mathbf{k}'}\,\phi^{(\lambda)}(\mathbf{k},\mathbf{k}')\Bigg|_{\mathbf{k}'=\mathbf{k}},$$

where

$$\phi^{(\lambda)}(\mathbf{k},\mathbf{k}') = \mathrm{Im}\{\ln[\det S^{(\lambda)}(\mathbf{k},\mathbf{k}')]\}$$

is the geometric quantum Berry phase, and

$$S_{mn}^{(\lambda)}(\mathbf{k},\mathbf{k}') = \langle u_m^{(\lambda)}(\mathbf{k})|u_n^{(\lambda)}(\mathbf{k}')\rangle$$

is the overlap matrix of lattice periodic wave functions $u^{(\lambda)}$ at different crystal momenta.

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$$|s_{\mathrm{int}}| = \Delta P^{(0)}(l_1+l_2)/(l_2\varepsilon_1^\infty + l_1\varepsilon_2^\infty),$$

and is obtained accounting for the general periodic boundary conditions $l_A E_A + l_B E_B = 0$ in the determination of ΔE and hence of s_{int}.

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