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First-Principles Theory of Polarization and Electric Fields in Ferroelectrics

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Three recently introduced approaches to the theoretical treatment of ferroelectrics and related materials in finite electric fields will be reviewed. First, the use of effective-Hamiltonian treatments that have been fitted to first-principles calculations for describing applied electric fields and even field-induced structural phase transitions at finite temperatures will be discussed. Second, a recently developed approach in which a systematic expansion of the free energy is truncated at a low order in the applied electric field, allowing for a mapping of the energy landscape as a function of polarization and of electric-field induced effects, will be reviewed. Third, a fundamental development of a direct method for treating insulators in finite electric fields within density-functional methods will be described. For each of these approaches, an example application is given.

The use of first-principles electronic-structure methods based on density-functional theory for the study of ferroelectric materials has been very successful in recent years [1–3]. Nevertheless, it has not been straightforward to treat the application of a homogeneous electric field to the material using these methods. The essential problem is that such methods are based on the Bloch theorem, which requires that the electron potential should be periodic under lattice translations, a condition that is not fulfilled in the presence of an electric field. In view of the of the fact that the response to an electric field is one of the first things one would like to know about a ferroelectric or piezoelectric material, this has been an important limitation of the theory.

The problem has not been very severe, however, because of the early development of methods for treating homogeneous electric fields in low order in perturbation theory [4, 5]. Such methods allow for the calculation of such quantities as the dielectric tensor and the dynamical effective charge tensor in the Bloch framework with a computational effort that is comparable with that of the ground-state solution itself. Moreover, the successful development of a first-principles theory of the electric polarization [6], which is conjugate to the electric field, has also ameliorated these problems. For example, the dynamical effective charge can be defined as the force that appears on an atom in linear response to an applied

electric field, but it can equivalently and more easily be computed as the first order change in polarization that occurs upon displacement of an atomic sublattice in the crystal.

Nevertheless, there are many situations in which one would like to be able to apply a finite electric field to a crystalline insulator, and to compute the various properties of the material directly in the presence of such a field. For example, certain ferroelectric materials may undergo a structural phase transition at a critical value of an applied electric field, and it would be virtually impossible to study such a situation using a perturbation expansion about zero field.

In this manuscript, I briefly review three approaches that have been used successfully in recent years to treat the existence of a finite, homogeneous electric field, starting from the most approximate and proceeding to the most rigorous and fundamental.

Effective-Hamiltonian Methods

In the effective-Hamiltonian approach [7, 8], one defines a reduced number of degrees of freedom per unit cell (typically, a ferroelectric mode vector and a displacement vector in each unit cell), and constructs a model Hamiltonian, written as a function of these reduced degrees of freedom, that reproduces the spectrum of low-energy excitations (ferroelectric soft modes and strains) for the given material as obtained from the ab-initio DFT-LDA calculations. One then arrives at a model, typically containing 10–20 parameters, that can be subjected to Monte Carlo (MC) or molecular dynamics (MD) simulations in order to determine the finite-temperature properties of the material. The coefficients of this model are then determined from the ab-initio calculations.

Within this approach, it is straightforward to apply an electric field to the system at the stage of doing the MD or MC simulations. The approximations involved are: (i) that the force that appears on an atom is just linear in the applied field, for fixed atomic coordinates; (ii) that the coefficient of linearity, the dynamical effective charge Z^*, is independent of distortion, and may be computed in the reference cubic structure; and (iii) that the higher (hard) modes may be neglected and that the truncations of the Taylor expansion made when constructing the effective Hamiltonian are justified.

We present here an example of the application of this method to $PbZrTiO_3$ (PZT) with $x = 0.5$ using an effective Hamiltonian that also contains terms to describe the B-site alloy disorder of this system [9, 10]. Figure 1 shows the behavior of the polarization of this system (u_x, u_y and u_z are proportional to the polarization components P_x, P_y and P_z) as an electric field is applied in the (111) direction. At zero field, PZT at $x = 0.5$ is a tetragonal crystal; we take the tetragonal axis along z. As the electric field is applied, the polarization tilts gradually at first from the (001) towards the (111) direction, as would be expected from perturbation theory. However, at a critical electric field of approximately 10^8 V/m, we find that the system undergoes a second-order phase transition in which the polarization direction "snaps" to align with the (111) axis. The lower panel shows that this behavior also generates sharp features in the piezoelectric response. In Ref. [10] we also consider the opposite case in which x is chosen so that the system is rhombohedral in zero field, and the electric field is applied along the (001) direction. Here the behavior is found to be more complicated, traversing a series of structures of different symmetry, and allowing for a wide region of electric field in which the piezoelectric response is enhanced.

Theory of Structural Response

Next, we consider a theory [11] which relaxes the various approximations involved in the effective-Hamiltonian approach and instead deals directly with the ab-initio calculations. In this approach, one still makes the approximation (i) above, namely, that that the force that
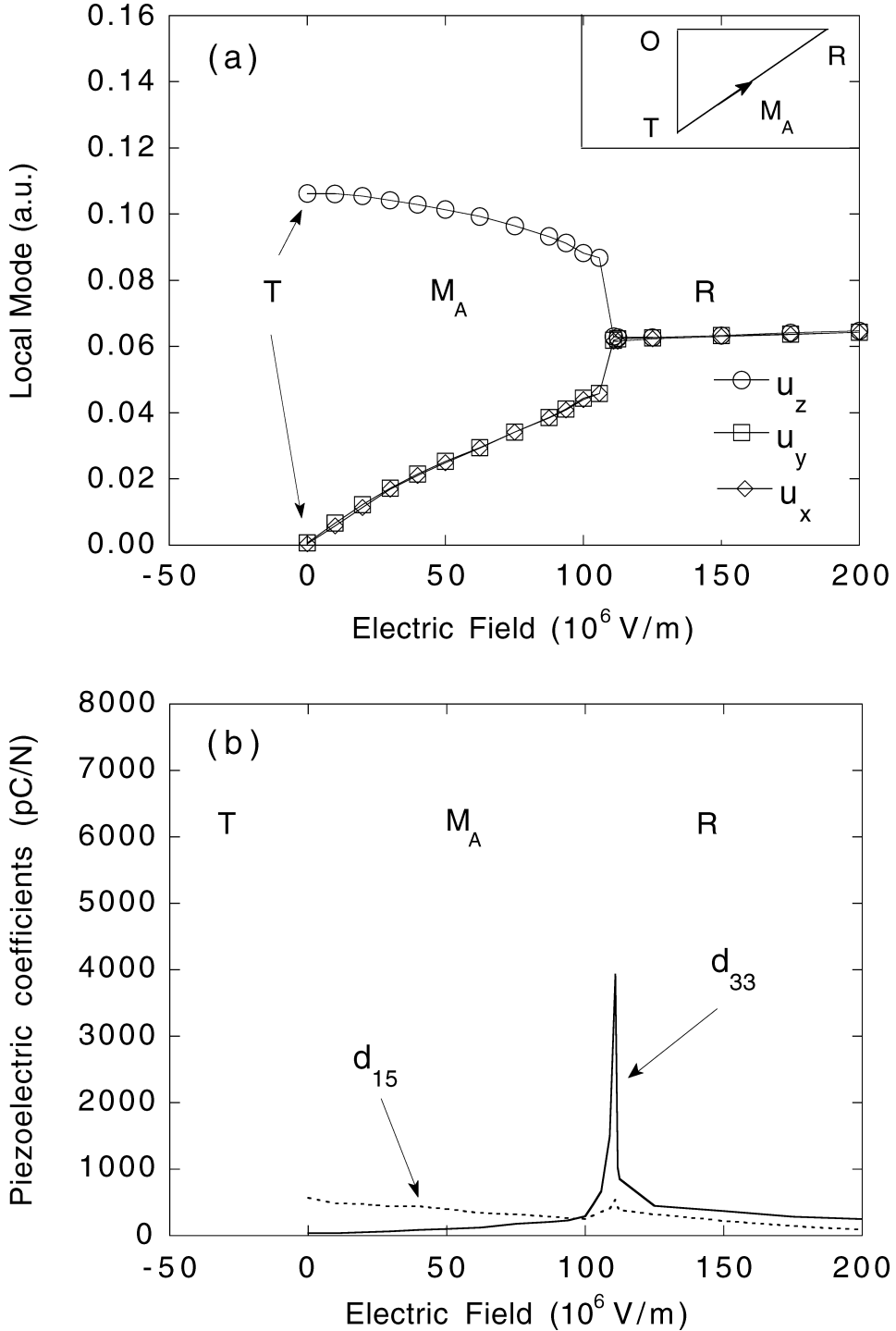
FIGURE 1 (a) Cartesian components u_x, u_x and u_z of the local-mode vector, and (b) d_{33} and d_{15} piezoelectric coefficients, as a function of the magnitude of the electric field applied along the pseudo-cubic [111] direction in disordered single crystals of PZT at $T = 50$ K. Insert illustrates the path followed by the polarization vector.
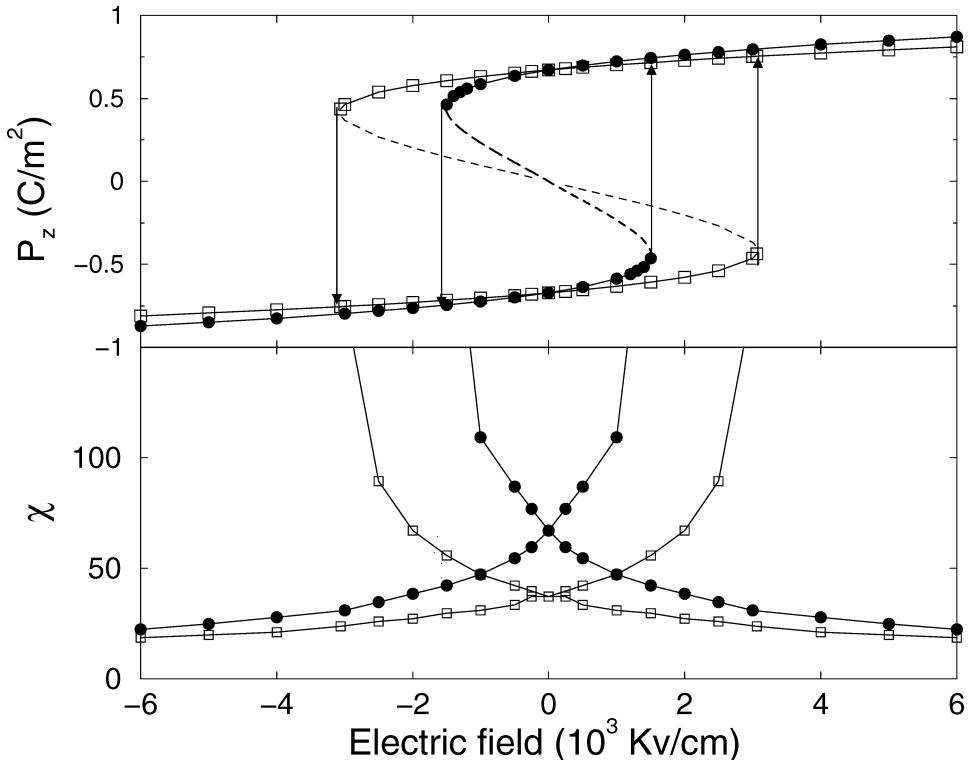
FIGURE 2 Calculated polarization-vs.-electric-field hysterisis loop (upper panel) and static susceptibility (lower panel) and static susceptibility of PbTiO$_3$ under stress-free condition (solid circles) and clamped-strain condition (open squares). Dashed line corresponds to a non-accessible state (a saddle point in the thermodynamic potential).

appears on an atom is linear in the applied field, but this is the only approximation. One thus treats the influence of the electric field on the *electronic* structure only to first order for fixed ionic coordinates, but treats the resulting structural distortions to *all* orders in perturbation [11]. This will be a good approximation in systems, like the perovskite ferroelectrics, that are dominated by one or more soft modes and for which the electronic gap is not much reduced by the structural distortions of interest.

Figure 2 shows the intrinsic hysteretic behavior of the polarization and susceptibility of tetragonal PbTiO$_3$ as a function of electric field applied along the tetragonal axis as calculated using this approach [11]. We identify the *intrinsic* coercive field (i.e., the one sufficient to cause *coherent* volume reversal of the polarization without barrier) of 1.5 MV/cm and 3 MV/cm for free-stress and clamped-strain elastic boundary conditions, respectively. (Of course, the true coercive field is determined by domain-wall pinning effects and will be much smaller.) Here again, there is an interesting discrete physical behavior that occurs at *finite* electric field that would be difficult to obtain via perturbative treatments around zero field. The corresponding piezoelectric responses, and studies of field-induced structural phase transitions similar to those of the previous Section, are also presented in Ref. [11].

Fundamental Theory of Insulators in Electric Fields

In recent work, Souza, Iniguez, and Vanderbilt [12], and independently and slight later, Umari and Pasquarello [13], have demonstrated a new method for the direct calculation

of the properties of a crystalline insulator in an electric field. In this approach, based on earlier work of Nunes and Gonze [14], the electronic one-particle density matrix is required to remain periodic and is expressed in terms of Bloch-like functions, despite the fact that these do not remain eigenstates of the Hamiltonian in the presence of the applied field. The formulation looks similar to the usual one, except that the energy functional contains new additional terms in which neighboring k-points in the Brillouin zone are coupled to each other in a way that does not take the conventional form of an expectation value of an operator. Nevertheless, the energy functional may be minimized by standard techniques, such as conjugate gradients, and quantities such as the Hellmann-Feynman forces may be computed in the usual way once the solution has been found.

There are subtleties associated with this approach that are connected with the fact that a crystalline insulator in a uniform electric field technically does not have a well-defined ground state, since the electron potential is unbounded from below, and this difficulty can give rise to an instability in the solution for the electron system. However, we have shown that this instability is connected with the density of k-points in the reciprocal space mesh in such a way that for any given mesh density, the solution remains stable up to a critical electric field that scales inversely with mesh density. In most cases, this allows the interesting range of electric fields to be covered by the calculations.

As an example, Table 1 shows the results of calculations of dielectric and piezoelectric constants of two III–V semiconductors obtained by finite differences. That is, we increase the electric field in small increments and compute the changes in the resulting forces, stresses, and polarizations, with internal displacements and strain either clamped or unclamped as appropriate. The Born effective charge is $Z^* = dF/dE$ (contrary to previous finite-difference approaches, we compute it as the derivative of the force F with respect to the electric field E, not polarization with respect to displacement). The dielectric constant is $\varepsilon_\alpha\beta = \delta_\alpha\beta + \chi_\alpha\beta$, where $\chi_\alpha\beta$ is the dielectric susceptibility and ε_0 is the vacuum permittivity. If the ions are kept fixed, this yields the electronic contribution ε_∞; if both electrons and ions are allowed to relax in response to the field, the static dielectric constant ε_{static} is obtained. The nonlinear quadratic susceptibility is $\chi^{(2)}_{\alpha\beta\gamma} = (2/\varepsilon_0)d^2 P_\alpha/dE_\beta dE_\gamma$, and we have computed it keeping the ions fixed. In the zinc blende structure, the only nonzero independent components of these tensors are Z^*_{11}, ε_{11}, and $\chi^{(2)}_{123}$. The "proper" piezoelectric coefficient γ_{14} can be computed as the derivative of the stress component σ_4 with respect to applied electric field E_1, allowing ionic positions to relax. It can be seen that reasonably good agreement is found between theory and experiment; the discrepancy presumably results mainly from the errors in the LDA approximation to the DFT theory.

Summary and Prospects

Several methods have been demonstrated here that may be used for calculating the properties of insulating crystals, such as ferroelectrics and piezoelectrics, in the presence of a static

TABLE 1 Computed Dielectric and Piezoelectric Properties of Two III–V Semiconductors Compared with Experimental Values

	GaAs (theo.)	GaAs (expt.)	GaP (theo.)	GaP (expt.)
$Z^*(e)$	2.00	2.07	2.10	2.04
ε_∞	11.9	10.9	9.4	9.0
ε_{static}	13.5	13.2	11.2	11.1
$\chi^{(2)}$ (pm/V)	134	166	66	74
$\gamma_{14}(e/a^2)$	−0.40	−0.32	−0.25	−0.18

homogeneous electric field. All of these are based on first-principles density-functional methods, but the first two approaches involve additional approximations, while the last one presented makes no approximations other than the usual ones of the local-density approximation and discrete k-point sampling. These methods therefore show considerable promise for allowing straightforward calculations of the properties of such systems in finite electric field, allowing especially for the study of nonlinear effects and phase transitions associated with a critical electric field that would be difficult or impossible to study via conventional perturbative techniques.

Acknowledgments

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