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First-principles based modelling of ferroelectrics

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The application of first-principles computational methods to the study of ferroelectric perovskites has greatly expanded our theoretical understanding of this important class of materials. These methods have most recently been applied to an increasingly wide range of ferroelectric materials, with special attention to their lattice dynamics, phase transitions, and dielectric and piezoelectric properties, and to the study defects such as surfaces.

Introduction

Ferroelectric (FE) materials are of growing importance for a variety of actual and potential applications. These include piezoelectric transducers and actuators, non-volatile ferroelectric memories, dielectrics for microelectronics and wireless communication, pyroelectric arrays, and non-linear optical applications.

The most important class of FE materials are the perovskite oxides ABO_3 (e.g., $BaTiO_3$). At high temperature these all share the paraelectric simple-cubic perovskite structure: metal A at the cube corners, metal B at the cube center, and O atoms at the cube faces. As the temperature is reduced, a structural phase transition into a FE state takes place, in which the B atom (usually a transition-metal atom) displaces off-center with respect to the surrounding oxygen octahedron, so that the material develops a spontaneous electric polarization P. In some materials (such as $PbTiO_3$) there is a single such transition, while in others (such as $BaTiO_3$ or $KNbO_3$) there is a sequence of several FE transitions in which the direction of P changes. Moreover, antiferrodistortive instabilities, involving a rotation of the oxygen octahedra, also occur in some of these materials (e.g., $PbZrO_3$, $SrTiO_3$).

The experimental and theoretical study of these structural phase transitions has a long history, much of which is reviewed in several standard reference works [1-3]. Until recently, the theoretical studies have been entirely of an empirical character; typically a model Hamiltonian (e.g., a Landau or spin model, or empirical lattice-dynamical model) is fitted to reproduce certain experimental features, and then used to predict new features or systematize the understanding. While this has been an extremely valuable approach, the development of computational methods in the electronic-structure community has led to a new class of first-principles approaches, based upon a full solution for the quantum-mechanical ground state of the electron system within the local-density approximation (LDA) to Kohn-Sham density-functional theory (DFT) [4]. In principle, these methods take as their only inputs the atomic numbers of the constituent atoms. Such methods hold the promise for providing chemically-specific information and understanding about the structural and electronic properties of the various perovskite materials. Indeed, the work of recent years, beginning only at the start of the present decade, has confirmed that this is the case. In fact, many details of the lattice dynamics and dielectric properties, the sequence of structural phase transitions, and even the transition temperatures can be predicted using first-principles calculations directly, or using models based on such calculations. The purpose of the present review is to summarize these developments.

Structural and electronic properties

The simplest direct applications of the first-principles approach involve computing the total energies, and ideally also the forces on each atom, as a function of the atomic coordinates as the system undergoes distortions from some reference cubic perovskite structure. Such distortions include displacements of one of the ionic sublattices, linear combinations of these ("frozen phonons"), or variations of lattice constant and other lattice strains. By mapping out the energy landscape using such an approach, it is possible to check for instabilities and identify the distorted ground-state structure (although strictly speaking only at T=0 and for a classical treatment of the ionic coordinates). LDA-DFT calculations of this type were first carried out using the linear augmented plane-wave (LAPW) method [5-13] and shortly afterwards by ultrasoft pseudopotential (USPP) [14-16], linear muffin-tin orbital (LMTO) [17-20], and norm-conserving pseudopotential (NCPP) methods. These calculations quickly proved their applicability to this class of compounds by confirming the existence of FE instabilities for such prototype materials as $BaTiO_3$ [5,6,8,14,15], $KNbO_3$ [7,9,10,12,15,17-20], and $PbTiO_3$ [6,8,15,16], and successfully predicted the correct symmetry of the T=0 ground-state structure in each case. Recent work has extended these studies to a wider variety of materials [11-13,15,17,18]. Frozen-phonon studies [5,7,8,11,12,15,18-20] were also able to identify the eigenvectors and frequencies of zone-center transverse optic (TO) modes, and especially to provide detailed knowledge of the FE soft mode.

The LAPW and LMTO methods use radial basis functions inside atom-centered spheres and other basis functions outside, while the pseudopotential methods use a plane-wave basis throughout; the former methods are (at least in principle) all-electron methods, while the latter approach facilitates the efficient and accurate calculation of forces. Generally the experience has been that the LAPW and USPP calculations are of high quality and are in very good agreement with each other where they have been carefully compared, and both are probably making errors that are small compared to the intrinsic errors of LDA-DFT. Calculations with the NCPP can also be of high quality, although unlike in the USPP method the semicore shells on the metal ions are typically treated as part of the frozen core, and the transferability of the pseudopotential may sometimes be compromised in order to obtain a computationally tractable plane-wave cutoff. The LMTO approach has also been successfully used in many applications, although in some cases there have been discrepancies (e.g. for phonon eigenvectors) relative to other methods and experiment. Recently, some authors have explored more approximate LDA-based schemes [21], or the use of ab-initio Hartree-Fock methods [22,23], but it is not clear that the structural properties should be expected to be of quite the same level of accuracy as in the previously-mentioned LDA-DFT approaches.

There is one shortcoming of the LDA-DFT calculations that should not be overlooked: they tend to make a small error (usually an underestimate on the order of 1%) in the predicted equilibrium lattice constant of the material. While a 1% error might seem small, it turns out that the FE instability is extraordinarily sensitive to the lattice parameter. For example, a reduction of the lattice parameter by 2% is enough to eliminate the FE state in $BaTiO_3$ entirely. Most workers have found that the results (for distortion amplitudes, spontaneous polarizations, and FE transition temperatures) are systematically in better agreement with experiment if one works at the experimental lattice constant, instead of at the theoretical equilibrium lattice constant. Unfortunately, this constitutes an unsatisfying retreat from the goal of a completely first-principles approach, free of experimental input. The consistency of the results of studies by a variety of techniques (LAPW, USPP, etc.) confirms that the lattice-constant error is a fundamental problem inherent in the LDA approximation to DFT, and not an artifact of any particular implementation. Recently, Singh has shown that use of the weighted-density approximation (WDA) in place of the LDA appears to give good systematic improvement in this respect, at the expense of only modest computational cost [12]. This is an important result, and it is to be expected that other groups will also try adopting the WDA scheme.

Polarization, dynamical charges, and origins of ferroelectricity

The salient feature of a FE material is the presence of a spontaneous polarization P, and it is clearly of the first importance to calculate this quantity and its variation with structural parameters. The first-order dependence of P upon atomic displacements and lattice strains are given by the dynamical (or Born) effective charges Z^* and the piezoelectric couplings c, respectively. While it has been known for some time how to compute such Z^* and from linear-response methods [24], the development of a direct method for computing P (and therefore its derivatives with respect to displacements or strains by numerical finite differences) by the authors of Ref. [25] had an important impact.

This method was immediately applied to study the dynamical effective charges of $KNbO_3$ by the authors of Ref. [9], with the remarkable result that the Z^*=9.13 for Nb is significantly larger than its nominal ionic value Z=5 (with a corresponding anomalous Z^* for oxygen motion along the Nb–O bond). This pattern of anomalous Z^* values was found to be a universal feature of virtually all of the ferroelectric perovskites [26], and its origin was traced to the borderline ionic-covalent character and specifically to the hybridization between O 2p and B-atom 3d or 4d orbitals in the ABO_3 material [9,10,26]. Subsequent work has more carefully characterized these anomalous Z^* values, especially their dependence upon structural parameters and their decomposition by band contribution [27-32]. Such investigations have also provided insight into the origin of the FE instability and its relation to the long-range Coulomb interactions [33,34] and to many-body electron correlation effects [35,36].

Linear-response studies of phonons

In the frozen-phonon approach, only the Brillouin zone center phonons are accessible from calculations on the bulk (five atom per cell) structure; zone boundary and other phonons at rational wavevectors are also available, although at increasing expense, from supercell calculations. The work of Ref. [24] demonstrated how to compute phonon properties on an arbitrary mesh of wavevectors, at least in the context of NCPP methods, and this approach was then extended to LAPW methods by Krakauer and coworkers [37]. This has made possible a much more systematic study of the phonon properties of the materials than would otherwise be possible.

In most cases, the analysis of the phonon spectrum has been carried out in the reference ideal cubic structure, so that the FE or other instabilities show up as imaginary phonon frequencies. For example, applying such an approach to $KNbO_3$ [32,38-40] one finds that the portion of the Brillouin zone at which imaginary frequencies (potential FE instabilities) occur comprises a set of three "sheets" surrounding the x-y, x-z, and y-z planes, consistent with a picture in which the FE dipoles associated with each unit cell are strongly correlated in longitudinal chains along the Cartesian axes. Similar results have been reported for the similar material $BaTiO_3$ [41,42]. On the other hand, for $PbZrO_3$ [43] and $SrTiO_3$ [44], the same approach demonstrates that both FE and antiferrodistortive instabilities are simultaneously present in the cubic reference structure, and nicely characterizes the portions of the Brillouin zone where each kind of instability is strongest.

A second application of this approach is to first identify the T=0 ground state structure by a careful total-energy minimization, and then apply the linear-response calculation to study the phonons in the ground-state structure. In this case, all of the frequencies must be real. A good example of this kind is a recent study of the rhombohedral ground-state structure of $KNbO_3$ [31].

Finite-temperature statistical properties: phase transitions

The methods discussed so far are essentially restricted to study the zero-temperature properties of the materials. Clearly it is of the first importance to see whether one can understand such features as the phase transition sequence and transition temperatures on a material-specific basis. A very successful approach to this problem has been the effective Hamiltonian approach [45-47]. Here, one defines a reduced number of degrees of freedom per unit cell (typically, a FE 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 (FE 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) [47-52] or molecular dynamics (MD) [53] simulations in order to determine the finite-temperature properties of the material.

This approach has been applied with considerable success to the FE materials $BaTiO_3$ [47,48], $PbTiO_3$ [52], and $KNbO_3$ [53], with the theory correctly reproducing the experimental phase transition sequence in each case. The T_c values for the cubic-to-tetragonal, tetragonal-to-orthorhombic, and orthorhombic-to-rhombohedral structural phase transitions in $BaTiO_3$ are obtained from the theory as 290K, 230K, and 197K, compared with experimental values of 403K, 278K, and 183K, respectively [47,48]. The corresponding values for $KNbO_3$ are 370K, 260K, and 210K, to be compared with experimental values of 701K, 488K, and 210K, respectively [53]. $PbTiO_3$ has only a single phase transition from cubic to tetragonal, for which the theoretical and experimental values are 660K and 763K, respectively [52]. It can be seen that the theoretical values tend to be too low, typically by 20% or so, but in the worst case by almost 50%. Given that the calculations are based almost entirely on first principles, taking no input from experiment (except for the experimental lattice constant), this is overall a satisfying level of agreement. Moreover, the calculations give other useful information about the nature (soft-mode vs. order-disorder) of the transitions and their latent heats, and the correlations, fluctuations, and dynamics [53] in the various phases. They can also be helpful in identifying the role of strain coupling in the FE transitions [54].

For more complex materials such as $SrTiO_3$ [49,50], $PbZrO_3$ [51], $CaTiO_3$ [50], and $NaNbO_3$ [50], one has antiferrodistortive instabilities competing with the FE ones. In $SrTiO_3$ one has reasonable agreement (130K theory vs. 105K experiment) for the cubic-to-tetragonal antiferrodistortive transition, but the simulation also shows FE phases below 70K [49,50]; however, when quantum fluctuations are taken into account, the former transition changes to 110K, and the FE phases disappear [55], in excellent agreement with experiment. In the more complex materials $PbZrO_3$, $CaTiO_3$, and $NaNbO_3$, the behavior is more complicated, and the predicted sequence of phase transitions does not always exactly follow the experimental one. Further work is needed to understand where the limitations of the theory lie, e.g., whether it is the LDA approximation to DFT itself that is inadequate, or whether the formulation of the effective Hamiltonian was oversimplified.

New directions

The materials used in real-world applications are complex in a variety of ways that challenge the theoretical community. For example, for many applications the behavior of the material under conditions of applied electric fields and strains is of primary importance. Thus, the study of the piezoelectric properties of the materials is now beginning, with a recent calculation on $PbTiO_3$ illustrating one way to proceed [56]. Many of the materials of interest are random solid solutions, e.g., PZT ($PbZr_{1-x}Ti_xO_3$), BST ($Ba_{1-x}Sr_xTiO_3$), or PMN ($PbMn_{1/3}Nb_{2/3}O_3$). Studies of the cation ordering and its consequences in such compounds are just beginning [57,58], and eventually the program of construction of an effective Hamiltonian and its use in MC or MD simulations will have to be carried through for these kinds of materials. Finally, the real materials are frequently ceramics (i.e., composed of randomly oriented crystallites) or films, and a critical role is often played by boundaries and defects of various kinds, including grain boundaries, surfaces, interfaces (e.g. with metallic contacts), and FE domain walls. The 180° domain boundary in $BaTiO_3$ has recently been studied using the effective-Hamiltonian approach [59], and studies of $BaTiO_3$ free surfaces have also appeared [60-62], but there is clearly much that remains to be done in this area.

Conclusions

In summary, first-principles based methods have been remarkably successful in modelling many of the physical properties of ferroelectric perovskite materials. These include the ground state structure, the spontaneous polarization and the related dynamical effective charges, the phase transition sequences and transition temperatures, and details of the lattice dynamics and of the dielectric and piezoelectric response. Future work will be needed to make the calculations even more accurate, ideally eliminating the errors associated with the small mismatch between the theoretical and experimental lattice constants; to extend the work to wider classes of materials, especially solid solutions; to expand the characterization of piezoelectric properties; and to study the role of defects, including surfaces, interfaces, grain boundaries, point impurities, and dislocations.

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