

Modeling of Ferroelectric Oxide Perovskites: From First to Second Principles

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Abstract

Taking a historical perspective, we provide a brief overview of the first-principles modeling of ferroelectric perovskite oxides over the past 30 years. We emphasize how the work done by a relatively small community on the fundamental understanding of ferroelectricity and related phenomena has been at the origin of consecutive theoretical breakthroughs, with an impact going often well beyond the limit of the ferroelectric community. In this context, we first review key theoretical advances such as the modern theory of polarization, the computation of functional properties as energy derivatives, the explicit treatment of finite fields, or the advent of second-principles methods to extend the length and timescale of the simulations. We then discuss how these have revolutionized our understanding of ferroelectricity and related phenomena in this technologically important class of compounds.

1. INTRODUCTION

The history of ferroelectricity started one century ago, when Valasek (1) discovered that Rochelle salt possesses a spontaneous polarization, $\mathbf{P}$, that can be reversed in a sufficiently large external electric field, $\mathbf{E}$, yielding hysteretic $\mathbf{P}$ – $\mathbf{E}$ loops similar to those known for magnetization versus magnetic field in ferromagnets. For some time, ferroelectricity remained an academic curiosity, restricted to hydrogen-bonded, water-soluble, and fragile crystals of modest interest [like potassium dihydrogen phosphate, KDP (2, 3)].

A major turn arrived in the early 1940s when barium titanate (BaTiO_3) was discovered as being a strong ferroelectric (4). On one hand, the simplicity of its cubic perovskite ABO_3 structure made it the prototypical material for fundamental studies of ferroelectricity. On the other hand, its stability and robustness opened the door to full exploitation of ferroelectrics in technological devices. This quickly gave rise to the emergence of an electro-ceramic industry focusing not only on ferroelectricity itself but also on the various related giant dielectric, piezoelectric, pyroelectric, or nonlinear optical properties of ferroelectrics. Over the years, studies evolved from the device to its integration into electronic chips with recurrent miniaturization steps first at the microscale during the 1990s and at the nanoscale from the 2000s.

From the 1940s, many efforts were devoted to the discovery of new ferroelectrics, not only among perovskites (PbTiO_3 , KNbO_3) but also in other classes of materials, such as IV–VI semiconductors like GeTe (5), V–VI–VII compounds like SbSI (6), or also organic polymers like PVDF (7). As beautifully summarized by Cross & Newnham in their brief article, “History of Ferroelectrics” (8), nowadays hundreds of compounds are known to be ferroelectric, most of them being nonperovskite and even nonoxide. Nevertheless, most device applications today still rely on oxides, which are the main focus of the present review.

Since the early stages, different theories have been proposed to explain the origin and mechanism of ferroelectricity. Following a series of seminal works by Mueller on Rochelle salt (9–12), a rather exhaustive description of ferroelectricity in perovskites was reported by Devonshire in the early 1950s (13–15), based on a phenomenological and macroscopic thermodynamical approach (hereafter referred to as Landau–Ginzburg–Devonshire or LGD). Later, Cochran (16, 17) in the United Kingdom and Anderson (18) in the United States provided independently a microscopic perspective. Relying on a possible competition between short-range (SR) and long-range (LR) dipolar forces, they introduced the concept of soft mode, giving the foundation of the model of displacive phase transitions. This view was later questioned by the eight-site model of Comès, Lambert & Guinier (19, 20), which was more in line with an order–disorder transition. Microscopic and macroscopic perspectives were elegantly combined by Lines in 1969 (21). These concepts were then further developed during the 1970s and 1980s from nonlinear shell-models, highlighting the fundamental role of the anisotropic polarizability of oxygen (22), as further included in the so-called polarizability model (23) still used today. At that time, the feeling was that most everything had been said about ferroelectricity!

At the same time and independently, first-principles density functional theory (DFT) was also developing. Relying on the fundamental theorems of Hohenberg & Kohn (24) and Kohn & Sham (25), DFT needed some time to become a practical and tractable approach. Key developments concerned the proposal of efficient methods for sampling the Brillouin zone (26, 27), the construction of pseudopotentials [norm-conserving (28) and ultrasoft (29)], and the determination of accurate quantum Monte Carlo data for the homogeneous electron gas (30) on which practical local density approximations (LDAs) were fitted (31). The Car–Parrinello method (32) and density functional perturbation theory (DFPT; 33, 34) were developed. At the end of the 1980s, most of the ingredients were already available to study ferroelectric phase transitions and related

functional properties. However, computational resources at that time were practically limiting drastically calculations to only a few atoms and electrons per unit cell.

In spite of a few precursor studies (35–38), the dawning of the still running era of first-principles modeling of ferroelectrics can likely be located in 1992 with the paper by Cohen on the “Origin of Ferroelectricity in Perovskite Oxides” (42). Since this milestone work, the symbiotic relationship between the atomistic modeling in material science from a broad perspective and the fundamental understanding of ferroelectricity and related phenomena has not stopped bearing mutual benefits. First-principles simulations have allowed researchers to make significant advances in the field of ferroelectrics: from the initial atomistic study of basic ferroelectric and piezoelectric properties of bulk compounds in the 1990s to multiferroics and nanostructures (thin films, superlattices or SLs) during the 2000s, and more advanced properties and mechanisms later (electro-optics, flexoelectricity, photovoltaics, or improper ferroelectricity among others). But, reciprocally, the study of ferroelectrics was at the origin of consecutive theoretical breakthroughs, with an impact going often well beyond the limit of the ferroelectric community—including the modern theory of polarization, maximally localized Wannier functions (MLWFs), finite-field techniques, advanced linear response schemes, or even second-principles methods.

Our purpose here is to provide a brief overview of the exciting progress realized during the past 30 years regarding the theory and modeling of ferroelectric oxide perovskites, highlighting some key breakthroughs and a few present challenges, as summarized in **Figure 1**. The topic is clearly much too broad to be exhaustive. We apologize in advance for eventual omissions and refer readers to more focused reviews for specific topics of interest when appropriate.

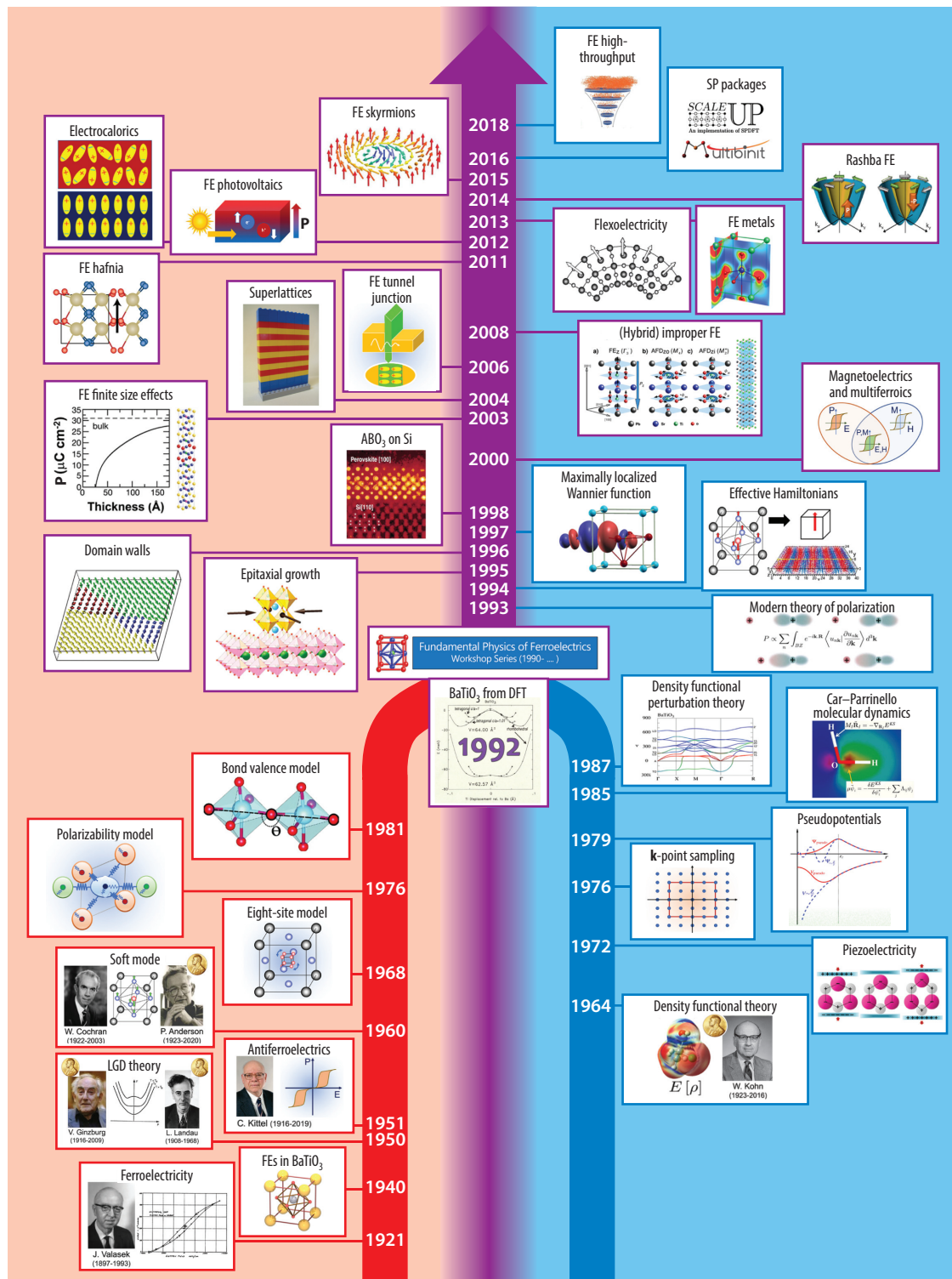
2. FIRST-PRINCIPLES METHODS

2.1. The Modern Theory of Polarization

The central quantity when addressing ferroelectrics is clearly their spontaneous polarization, $\mathbf{P}$, a magnitude that carries the meaning of electric dipole per unit volume. As such, $\mathbf{P}$ in insulating crystals is often defined in classical textbooks as the dipole moment per unit cell, i.e., the first moment of the total charge density distribution, $\rho(\mathbf{r})$, inside one unit cell, divided by the unit cell volume V_{cell} . However, as early as in 1974, Martin (53) showed that in an infinite periodic crystal with delocalized electrons, $\mathbf{P}$ cannot be derived solely from the knowledge of the periodic part of the charge density: Distinct choices of unit cell lead to different results while the ambiguity disappears only when fixing the crystal surfaces. In the early 1990s, this raised questions such as to what extent $\mathbf{P}$ is a bulk property and how it can be accessed from usual calculations with Born–von Karman (BvK) boundary conditions that only provide access to the periodic part of the wave function and density.

A first conceptual advance was achieved by Resta (54), who suggested that rather than considering the polarization as a static, equilibrium property of the crystal in a given state, a more dynamical definition can be considered, focusing on the change of $\mathbf{P}$ during an adiabatic evolution of the system between two different states. On one hand, this aligns with the way $\mathbf{P}$ is experimentally measured in hysteresis loops—integrating the current going through the sample under $\mathbf{P}$ reversal—or evolves in response to external perturbations (dielectric, piezoelectric, or pyroelectric tensors). On the other hand, different formulations were already available to compute derivatives of the polarization such as the Born effective charges using DFPT, providing a pioneering estimate of $\mathbf{P}$ in the linear regime (55).

The breakthrough arrived in 1993 when King-Smith & Vanderbilt (56) formulated $\mathbf{P}$ as a Berry phase (57) of the Bloch wave functions when the wave vector performs a closed loop across the Brillouin zone. Subsequently (58), they related that formulation to the charge accumulated at the



(Caption appears on following page)

Figure 1 (Figure appears on preceding page)

Timeline with some key breakthroughs regarding the study of FE oxides (*red*), the development of first- and second-principles methods (*blue*), and combining them (*magenta*). 1921 Ferroelectricity graph adapted with permission from Reference 1; copyright 1921 American Physical Society. 1964 Density functional theory graph adapted with permission from Reference 39; copyright 2019 John Wiley & Sons. 1979 Pseudopotentials panel from https://en.wikipedia.org/wiki/Pseudopotential#/media/File:Sketch_Pseudopotentials.png (public domain). 1985 Car–Parrinello molecular dynamics panel adapted with permission from Reference 40; copyright 2015 Springer. 1987 Density functional perturbation theory panel adapted with permission from Reference 41; copyright 1999 American Physical Society. 1992 BaTiO₃ from DFT panel adapted with permission from Reference 42; copyright 1992 Springer Nature. 1993 Modern theory of polarization panel adapted with permission from Reference 43; copyright 2012 Elsevier. 1994 Effective Hamiltonians panel adapted with permission from Reference 44; copyright 2004 American Physical Society. 1995 Epitaxial growth panel adapted with permission from Reference 45; copyright 2014 by Springer Nature. 1996 Domain walls panel adapted with permission from Reference 46; copyright 2015 American Physical Society. 1997 Maximally localized Wannier function panel adapted with permission from Reference 47; copyright 2008 American Physical Society. 1998 ABO₃ on Si photo reproduced with permission from Reference 48; copyright 1998 American Physical Society. 2003 FE finite size effects panel adapted with permission from Reference 49; copyright 2003 by Springer Nature. 2008 (Hybrid) improper FE panel adapted with permission from Reference 50; copyright 2008 by Springer Nature. 2013 Flexoelectricity panel adapted with permission from Reference 51; copyright 2006 American Physical Society. 2014 Rashba FE panel adapted with permission from Reference 52; copyright 2020 by Springer Nature. Photos of J. Valasek, V. Ginzburg, L. Landau, and W. Kohn reproduced with permission from AIP Emilio Segrè Visual Archives. Photo of C. Kittel reproduced with permission from National Academy of Sciences. Photo of W. Cochran reproduced with permission from the Royal Society. Photo of P. Anderson from https://es.wikipedia.org/wiki/Philip_Warren_Anderson#/media/Archivo:Andersonphoto.jpg (public domain). Abbreviations: DFT, density functional theory; FE, ferroelectric; LGD, Landau–Ginzburg–Devonshire; SP, second principles.

surface of the crystal and highlighted some important consequences of what was emerging as the modern theory of polarization (MTP). One first outcome of this theory is that the Berry phase polarization is not a unique value but a multivalued quantity, determined modulo a quantum $e\mathbf{R}/V_{\text{cell}}$ (where $\mathbf{R}$ is a unit cell lattice vector and e is the electron charge) that physically corresponds to the transfer of one electron from one to the opposite surface of the crystal. A second key result is that for the purpose of calculating $\mathbf{P}$, the delocalized electron density can be seen as a set of quantized point charges, $-e$, located at the corresponding centroids of localized Wannier functions. A third fundamental consequence is that in line with the fact that in DFT the exchange–correlation functional is a priori a functional of the density everywhere (i.e., in the bulk and at the surface), for systems with BvK boundary conditions it should be a priori formulated as a density–polarization functional theory, involving both the periodic density and the polarization (59, 60). Generalization of the Berry phase formalism to strongly correlated systems has also been reported (61).

First applied to KNbO₃ (62), the MTP was quickly made available in many DFT software packages and applied to many systems, providing results in good agreement (i.e., a few percent) with experimental data. $\mathbf{P}$ being a multivalued quantity, proper computation of the spontaneous polarization might require some special technical care (63), especially when the polarization is large or the quantum is small—i.e., in large unit cells. A beginner’s guide to the MTP addressing this issue is provided in Reference 43.

The foundation of the MTP in terms of mathematical concepts like Berry phases, and the closely related Berry connections or Berry curvatures, allowed the establishment of a bridge with the field of the two-dimensional quantum anomalous Hall state or topological insulators. It has been also at the basis of many other theoretical developments, such as the “modern theory of orbital magnetization” (64), the theory of flexoelectricity (65), or the computation of shift currents in photovoltaic effects (66). It is beyond the scope of the present review to summarize all the details and developments, but the interested reader can find more details in References 67–69.

Another important follow up of the MTP is the computation of MLWFs (70). Wannier functions form a set of functions spanning the same space as the Bloch orbitals: Whereas the latter are localized in reciprocal space (attached at a given $\mathbf{k}$ vector), the former are localized in real space (attached at a given $\mathbf{R}$ vector). As such, Wannier functions are an appealing concept that

has been used, for instance, to design computational methods scaling linearly with the size of the system (71, 72) and has received a renewal of interest with the MTP (58). Wannier functions correspond to a unitary transformation of the Bloch states from which they can be derived a priori. The main problem is that they cannot be uniquely defined due to the phase indeterminacy of the Bloch orbitals. MLWFs elegantly solve that problem by fixing the phase in order to maximize the localization in real space. This opened the door to practical computation of MLWFs and their further use for many purposes (for a complete survey, see 73).

2.2. Finite Field Approaches

Determining how a ferroelectric material behaves under a finite electric field is another problem of fundamental importance, not only because ferroelectricity relies on the possibility of switching $\mathbf{P}$ in an external bias but also more broadly because the ferroelectric state is strongly dependent on the electrical boundary conditions. As previously evoked, first-principles modeling of periodic crystals makes use of BvK boundary conditions and Bloch theorem. Although such a framework is fully compatible with atomic displacements or homogeneous strains and the computation of related energy derivatives (interatomic force constants or IFCs, elastic constants) from finite difference techniques, it does not allow application of a finite homogeneous field $\mathbf{E}$. In the scalar-potential gauge, $\mathbf{E}$ is indeed described by a linear potential that (a) breaks the crystal periodicity so that Bloch theorem does not apply and (b) is not bounded from below so that, strictly speaking, there is no ground state owing to the interband tunneling (Zener effect).

A formalism circumventing the previous issues and providing access to the structural response of a periodic system to a finite homogeneous electric field was first proposed in Reference 74. A fundamental solution to perform real finite-field DFT calculations came shortly after from a series of papers building on the following observations. First, when switching on an adiabatically moderate electric field on an insulating crystal, the characteristic tunneling time can be exponentially long, so the state is well defined for practical purposes (69). Second, in the long-lived metastable states, the one-particle density matrix and, therefore, the charge density and all the other one-particle expectation values remain periodic, although the potential itself is not (75). An electric enthalpy functional for periodic systems was introduced (76) and variationally minimized by perturbation methods (77). Later, the method was extended to treat finite electric fields by Umari & Pasquarello (78) and Souza et al. (75, 79) by an iterative minimization of the electric enthalpy in a uniform grid of $\mathbf{k}$ points. Still, the method is practically limited to relatively small $\mathbf{E}$ because the drop of potential over the whole BvK supercell defined by the $\mathbf{k}$ -point sampling must remain smaller than the electronic bandgap to avoid Zener breakdown.

Working at fixed $\mathbf{E}$ appears at first appealing to model the behavior of a ferroelectric capacitor under finite bias. Unfortunately, such an experimental setup fixes the applied voltage V rather than $\mathbf{E}$, which further depends on the interface properties. As a seminal example, even in a capacitor in short circuit, $\mathbf{E}$ does not necessarily vanish owing to the finite screening length of the electrodes (49). Furthermore, in a layered structure, the field would change from one layer to another. Based on this, it was proposed by Stengel et al. that working instead at finite electric displacement field ($\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$) presents several advantages (80). (a) It corresponds to a clear experimental setup of a capacitor in open circuit with fixed value of the free charge on the surfaces; (b) $\mathbf{D}$ is constant throughout insulating supercells (81); (c) it makes the force-constant matrix of the quasi-one-dimensional SL short ranged in real space. This locality principle implies that one may expect the individual layer polarizations to depend only on the local compositional environment comprising the layer itself and a few nearby neighbors (82); (d) the treatment of electrostatic effects is rigorous, even in nonobvious charged mismatched systems that appear in

polar interfaces (83). In practice, the implementation of fixed $\mathbf{D}$ is relatively straightforward in any code already implementing the fixed $\mathbf{E}$ method. Furthermore, fixed $\mathbf{D}$ can even be imposed without any implementation working in a slab configuration and introducing virtual atoms monitoring the surface charge density (84, 85).

Finally, although it does not correspond to a clear experimental setup, some efforts have also been devoted to the computation of crystal properties at constant polarization in order to bridge first-principles calculations with the traditional LGD approach (13–15). A first step in this direction was taken by Fu & Cohen, while studying the polarization rotation in BaTiO₃ (86), but the exact approach was introduced by Diéguez & Vanderbilt (87), building upon some approximations formerly introduced by Sai et al. (74).

2.3. Functional Properties as Energy Derivatives

Ferroelectric materials are attractive not only for their switchable spontaneous polarization but also for the way the latter can be tuned by external fields (e.g., electric, magnetic, strain), yielding attractive functional properties (e.g., dielectric, piezoelectric, magnetoelectric, electro-optic, etc.). These can be formulated as derivatives of the energy and, as such, are directly accessible from first principles using either finite differences (frozen-phonon or finite-field approaches) or a linear-response formalism.

Second-energy derivatives with respect to atomic displacements and electric fields are associated with the force constant matrix, Φ (and related IFCs and phonon frequencies, ω), and Born effective charges (Z^*), as well as optical (ϵ^∞) and static (ϵ^0) electric permittivity (see **Table 1a**). They can be accessed from finite differences but have also been available from DFPT since the late 1980s (33, 34, 60). In ABO₃ perovskites, computations of Z^* highlighted strongly anomalous values, in line with giant LO–TO (longitudinal optical–transverse optical) splittings (92) and rationalized in terms of their mixed ionic–covalent character (93, 94). Then, determination of phonon dispersions curves (41, 95) and IFCs in real space (96) is the perfect tool to identify not only ferroelectric and other structural instabilities but also the kind of atomic correlations required to produce them (41, 96, 97). Also, the prediction of the static dielectric constant (60) proved useful in the search of new high- κ dielectric materials (98). Beyond second-energy derivatives, third-energy derivatives are also accessible from DFPT by making use of the $(2n + 1)$ theorem (99, 100). As

Table 1 (a) Physical properties related to second-energy derivatives with respect to atomic displacement (τ), homogeneous strain (η), and electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields: force constant matrix (Φ), elastic tensor (C), dielectric permittivity (ϵ), magnetic permeability (μ_m), Born effective charge (Z^*), magnetic effective charge (Z_m^*), piezoelectric (e) and piezomagnetic (q) tensors, magnetoelectric tensor (α), and atom-strain coupling constant (γ). (b) Physical properties related to spatial dispersion of some second-energy derivatives (88): spatial dispersion of the force constant matrix ($\Phi^{(1)}$), acoustical activity ($\mathcal{D}$; 89), natural optical activity (G ; 90), effective quadrupoles (Q ; 91), flexo force-response tensor ($\bar{C}$), and flexoelectric tensor (μ)

a	τ	η	$\mathbf{E}$	$\mathbf{B}$
	τ	η	Z^*	Z_m^*
	Φ	γ	e	q
	γ	C	ϵ	α
	Z^*	e	ϵ	α
	Z_m^*	q	α	μ_m

b	τ	η	$\mathbf{E}$
	τ	η	$\mathbf{E}$
	$\Phi^{(1)}$	$\bar{C}$	Q
	$\bar{C}$	$\mathcal{D}$	μ
	Q	μ	G

such, nonlinear optical susceptibilities, Raman tensors, and electro-optic coefficients (101, 102) are nowadays also directly available from first principles, as, for instance, implemented in ABINIT (103).

Another useful feature of ferroelectric perovskites is their electromechanical piezoelectric response exploited in numerous devices from fuel injections, inkjet printings, or microphones to ultrasonic devices for communications or medical diagnosis or including also energy harvesting applications. The direct and converse piezoelectric effects were discovered by the Curie brothers and Lippmann in 1880–1881 (104; i.e., even before ferroelectricity). As early as 1972, Martin argued that piezoelectricity is a well-defined bulk property of insulating crystals (91), and pioneering first-principles calculations were already reported in 1983 by McKitterick (105). Mathematically, piezoelectricity is quantified by a third-order rank tensor and various constants are defined depending on the independent variables that are considered (106). The piezoelectric tensor e_{ij} (using Voigt notations) corresponds to a mixed second derivative of the energy with respect to macroscopic electric field and strain. As such, it can be seen as the change of polarization linearly induced by a macroscopic strain (η) in zero field or, reciprocally, as the stress induced by an electric field at constant strain. Here, polarization and electric field must be interpreted as reduced quantities in order to yield the proper piezoelectric tensor, as measured when controlling the voltage across the sample (106, 107). It typically includes purely electronic and relaxed ion contributions. The Berry phase theory of polarization opened the door to the determination of e_{ij} from finite difference of polarization under finite strain: The method, initially exemplified on ZnO (108), was first applied to ferroelectric PbTiO_3 in Reference 109. Alternatively, e_{ij} was also accessible early on from DFPT as the stress induced under finite electric field. The treatment of the strain in DFPT is, however, less obvious than that of other perturbations. A first canonical-transformation approach was provided by Baroni, Giannozzi & Testa for the computation of elastic constants (110). A metric tensor formulation of the strain was more recently proposed by Hamann et al. (111) and implemented in the ABINIT software (103), providing routine access to all fixed- and relaxed-ion elastic and piezoelectric coefficients from DFPT (107).

Like piezoelectricity, flexoelectricity is another important coupling property (65). Although the former describes the linear coupling between electric polarization and strain and arises only in noncentrosymmetric materials, the latter relates to the linear coupling between electric polarization and a strain gradient and is always symmetry allowed. A first extended theory of flexoelectricity was reported by Tagantsev in the mid-1980s (112, 113). It has since been reexamined in the context of first-principles simulations under the light of the MTP. Whether flexoelectricity is a bulk property, like piezoelectricity, or depends on the details of the sample surface has been the matter of a lively debate over the years (112, 114, 115). Later works have corroborated the latter hypothesis, via both analytical derivations (116) and full-fledged first-principles calculations (117). The first attempts to compute some of the flexoelectric coefficients of BaTiO_3 and SrTiO_3 were done in supercells in which a longitudinal strain variation of cosine form was imposed (118). Later, Hong & Vanderbilt (119) and Stengel (120) independently tackled the problem of the computation of the flexoelectric tensors fully from first principles. Both approaches are complementary and arrived consistently to a nearly complete framework. Although the former authors relied on the long-wave analysis of induced dipoles, quadrupoles, and octupoles in the spirit of former works (91, 114), Stengel based his approach on the quantum mechanical probability current response to a long-wavelength acoustic phonon, accessible from DFPT. Building on this fundamental theory, and incorporating a number of further developments, a practical formulation was established a few years later. In Reference 88, the flexoelectric coefficient is formulated as a second derivative of the polarization response to an acoustic phonon with respect to the wave vector q . It can therefore be regarded as the spatial dispersion of the piezoelectric effect, because the latter occurs at first order in q . Appearing as a higher-order derivative of the energy, it requires judicious use of the

$(2n + 1)$ theorem to limit the computational cost (88); in its current ABINIT implementation (103), such a cost is comparable with the calculation of e_{ij} . This very elegant formulation is moreover not restricted to flexoelectric coefficients but opens the door to computations of various other physical quantities related to a spatial gradient of any external field starting from the response to homogeneous fields (see **Table 1b**). These include, for instance, effective quadrupoles as introduced by Martin (91), which were recently revealed to improve the interpolation of the phonon dispersion curves of piezoelectric crystal in the long-wavelength limit (including quadrupolar terms going beyond the usual dipole–dipole term in the description of LR electrostatic interactions; 121) and for the description of electron–phonon interactions beyond Frölich (122).

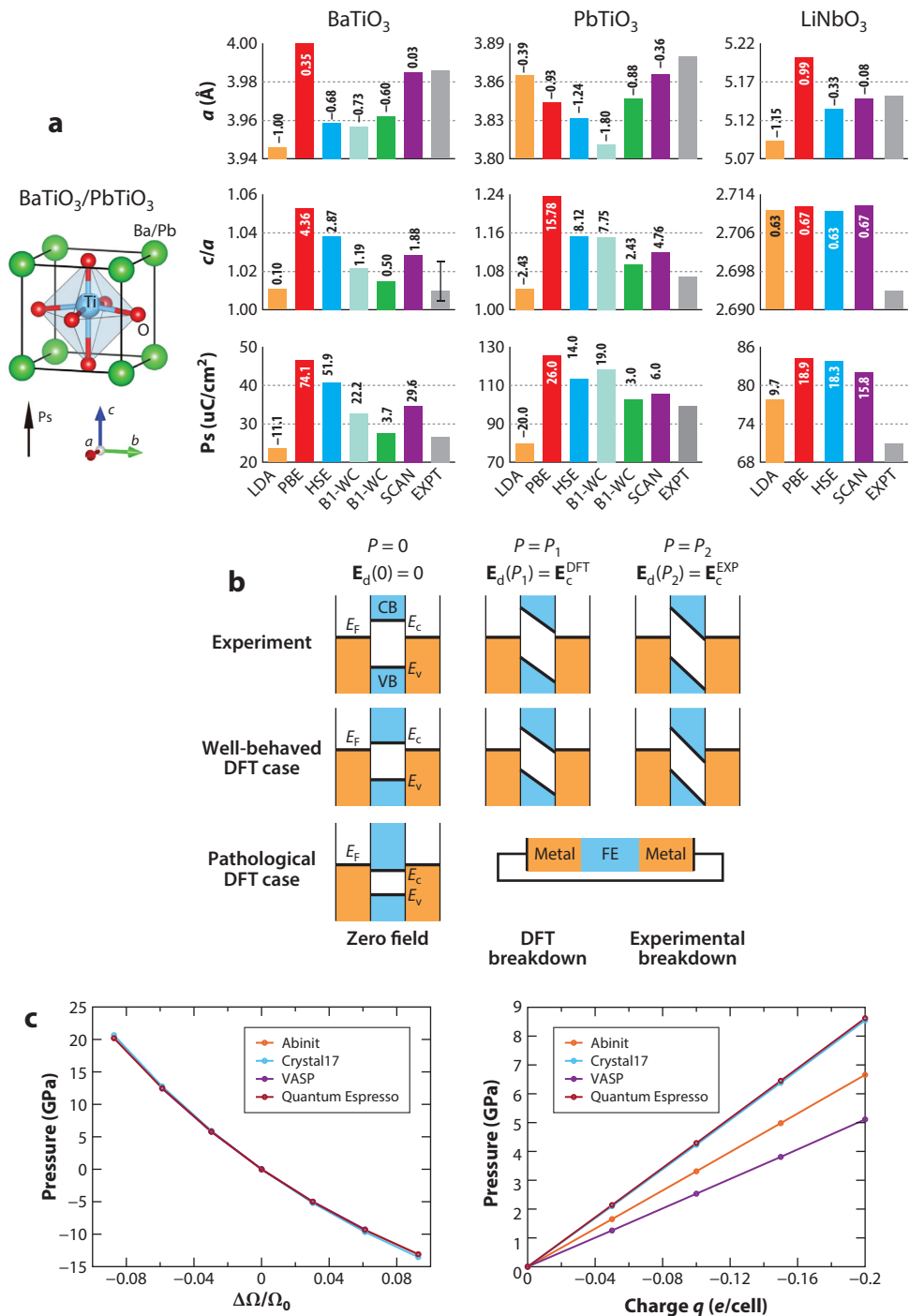
Finally, let us mention that the magnetoelectric effect is another central phenomenon that has known a renewed interest since the early 2000s. The linear magnetoelectric coefficient α_{ij} appears as a second derivative of the energy with respect to electric and magnetic fields and can be seen as the change of polarization linearly induced by a magnetic field (or reciprocally as the linear change of magnetization in a finite electric field). Pioneering formulation of the ion and strain contributions to α_{ij} was reported by Íñiguez and colleagues using a linear-response formalism and accessing quantities from finite differences (123, 124). Bousquet et al. (125) then provided further access to the electronic spin contribution from a finite magnetic field approach. Contributions of the orbital magnetization have been formulated later with the emergence of the modern theory of magnetization (126, 127). Although α_{ij} can be readily accessed nowadays from finite differences using the previous approaches, some advances have been performed very recently in order to access magnetic responses directly from DFPT (128, 129).

Nowadays, various functional properties are thus directly accessible from first principles providing insight into their microscopic origins, suggesting guiding rules to improve them and allowing researchers to make valuable predictions. However, this remains restricted to intrinsic properties at zero Kelvin. Due to the temperature dependence of their polar soft mode, the relaxed ion contribution of many properties (dielectric, piezoelectric, magnetoelectric, electro-optic) is diverging around the phase transition temperature so that better comparison with experiment motivates going further and accessing these at finite temperatures. This step has been undertaken with second-principles methods, presented in Section 3.

2.4. Discussion and Perspectives

DFT methods have acquired such a level of maturity that they permit the search for new ferroelectrics from high-throughput calculations (130, 131). More globally, huge materials databases compiling DFT results—such as the Materials Project (132)—have been under development since a few years ago. From these, data mining can be performed to select materials for a given application (133). Initially restricted to basic properties (e.g., crystal structure, electronic band structure), these databases have recently been extended to include various energy derivatives. This was made possible thanks to the high level of numerical precision of modern DFT methods (134). But one recurrent question concerns the level of accuracy of such predictions (i.e., how prediction compares to experimental data).

First-principles DFT methods have been applied to various ABO_3 perovskites, most often with good success. At the structural level, the usual DFT trends apply: The LDA tends to underestimate the volume of the cubic phase by 1–2%, whereas generalized gradient approximation (GGA) overestimates it similarly (135; see **Figure 2a**). At first sight, such a small error might appear reasonable. However, the ferroelectric instability is extremely sensitive to strain (i.e., strong polarization–strain coupling). As such, the small volume underestimate in LDA is enough to significantly decrease or eventually suppress the ferroelectric distortion (137), as already highlighted



(Caption appears on following page)

Figure 2 (Figure appears on preceding page)

Despite the indisputable success of first-principles simulations in the prediction of functional properties of FE oxides, special technical care must be taken before applying them in some cases. (a) Some functionals, such as the Perdew–Burke–Ernzerhof parametrization of the generalized gradient approximation (PBE–GGA), lead to an overestimation of the unit cell volume. In some cases, like PbTiO_3 , this yields an erroneous supertetragonal structure with a concomitant enhancement of the polarization of up to 26% with respect to the experimental value. (b) Schematic band alignment in a typical metal–FE–metal capacitor in short circuit. In the paraelectric state (*left column*), due to the DFT bandgap problem, the Schottky barrier ϕ_n is underestimated and can eventually produce pathological situations in which $\phi_n < 0$. In the FE state ($P \neq 0$; *central and right column*) under incomplete screening, the DFT bandgap problem is additionally responsible for a lowering of the breakdown field from E_c^{EXP} to E_c^{DFT} . If the residual depolarizing field E_d associated with the ground-state polarization exceeds E_c^{DFT} , a spurious transfer of electrons from the metal to the FE conduction bands will be observed at the interface and produce unphysical results. (c) Although different DFT softwares consistently reproduce the evolution of pressure with the unit cell volume (Ω) in neutral ($q = 0$) cubic BaTiO_3 , they do not similarly predict the evolution of the pressure with the doping charge q at the relaxed volume (Ω_0): The result depends on the convention chosen to define the reference energy. Panel *a* adapted from Reference 136; copyright 2017 American Physical Society. Abbreviations: CB, conduction band; DFT, density functional theory; E_c , bottom of the conduction band; E_F , Fermi energy; E_v , top of the valence band; FE, ferroelectric; VB, valence band.

in the early work of Cohen & Krakauer (138). This affects the relative stability of distinct phases and further impacts ferroelectric transitions temperatures (139, 140), as deduced from second-principles calculations based on LDA data. Furthermore, the volume overestimate linked to PBE (Perdew–Burke–Ernzerhof)–GGA tends to promote an erroneous supertetragonal ground state for PbTiO_3 ($c/a^{\text{PBE}} = 1.239$ versus the $c/a^{\text{exp}} = 1.071$ in PbTiO_3 ; 141) so that this functional should be avoided. A weighted density approximation (WDA) was proposed as a potential valuable alternative to the volume problem (142), but in the end it did not reveal a suitable solution. The origin of the PBE functional problem has been assigned to the exchange energy and has been corrected in the Wu–Cohen (WC; 141) GGA and PBEsol (PBE functional revised for solids)–GGA functionals (143), which appear today as the most valuable choices. The recently developed general-purpose strongly constrained and appropriately normed (SCAN) meta-GGA functional might reveal a valuable alternative (136, 144, 145). A recent comparison of available functionals is reported in Reference 146.

Another typical drawback of LDA and GGA functionals is the Kohn–Sham bandgap underestimation (see **Figure 2b**). Although not necessarily problematic for the study of bulk compounds, it can give rise to pathological situations when considering heterostructures (85). Hybrid functionals can provide a valuable alternative at reasonable computational costs. However, popular hybrid functionals like the so-called B3LYP, nonlocal PBE0 (147), or HSE (148) suffer from the same problem as the PBE–GGA they are based on (i.e., overestimation of the ferroelectric distortion). A valuable alternative is the so-called B1–WC functional (149) that is based on the WC–GGA and was specially designed for ferroelectric oxides.

3. SECOND-PRINCIPLES METHODS

Related to their multifunctional character, basic features of ferroelectrics are their structural phase transitions and the related strong dependence of their functional properties with temperature. In principle, the finite temperature behavior of materials is accessible from first-principles molecular-dynamics simulations since the early stage of DFT (150). Nowadays, however, such simulations remain practically limited by computational resources to very small length scales (a few hundreds of atoms per cell) and timescales (a few picoseconds), as sketched in **Figure 3a**. This prevents realistic first-principles study of ferroelectrics at finite temperature that would require large unit cells to accommodate random thermal fluctuations. The bottleneck of first-principles molecular dynamics is the recurrent time-consuming resolution of the quantum electronic problem at each time step.

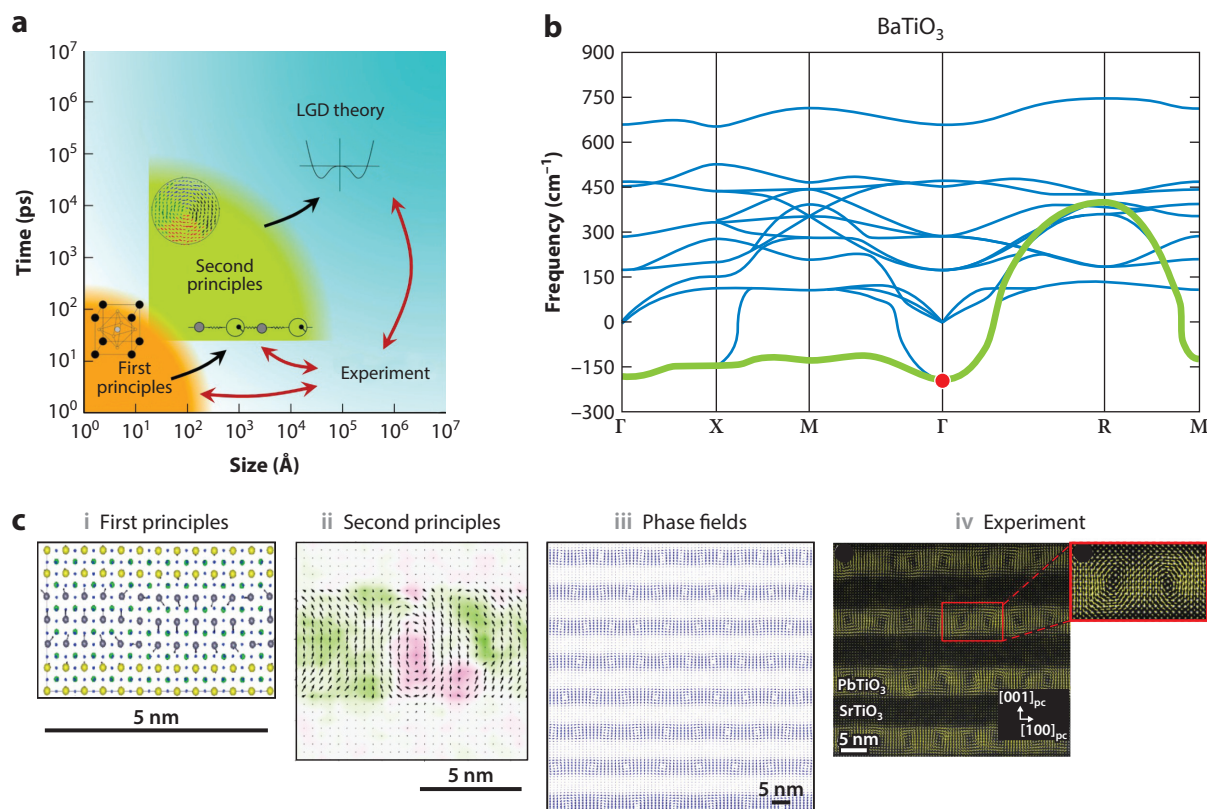


Figure 3

(a) Sketch with the different length and timescales affordable with the variety of theoretical schemes presented in this review. Arrows indicate the interconnection of the methods. First-principles methods with atomic resolution (represented by the balls and sticks cartoon), feed second-principles models in which only some degrees of freedom are considered (for instance, the soft mode in every unit cell, represented by the arrows or the springs in the cartoons). Parameters for the phenomenological LGD methods can be determined from atomistic methods. The arrows in red stress the interconnection between experiments and theories at the different levels. (b) Calculated phonon dispersion relations of BaTiO_3 along various high-symmetry lines in the simple cubic Brillouin zone. Simple LGD models focus on the polar soft mode at the Γ point (filled red dot). Model Hamiltonians are built on the lattice Wannier function related to the phonon branch associated with the relevant unstable mode (solid green line). Effective atomic potentials consider all the possible modes (i.e., rely on the full phonon dispersion curves). (c) Simulations on the same $\text{PbTiO}_3/\text{SrTiO}_3$ superlattice system using different methods. The horizontal line at the bottom of each subpanel underlines the different size scales affordable within each method. The theoretical results are in full agreement with the experimental observations. Panel a adapted from Reference 151; copyright 2012 John Wiley & Sons. Panel b adapted from Reference 41. Panel c, subpanel i, adapted with permission from Reference 152; copyright 2012 American Physical Society. Panel c, subpanel iii, provided by Z. Hong (unpublished). Panel c, subpanel iv, adapted with permission from Reference 364; copyright 2016 Springer Nature. Abbreviation: LGD, Landau–Ginzburg–Devonshire.

One option is to look for more efficient DFT methods (153). Another practical way to overcome the problem and perform lattice dynamical simulations at larger length- and timescales is to work with effective atomistic models, integrating out the electronic degrees of freedom and providing a simple parametric description of the Born–Oppenheimer energy surface in terms of structural degrees of freedom, to be used in further molecular-dynamics or Monte Carlo simulations. This is the basic idea underlying classical atomistic models that have been extended in chemical physics, material science, and biophysics. For decades, the parameters of such models have been empirically fitted. What we coined here as a second-principles approach

consists of building effective models in a multiscale perspective, determining parameters directly from first-principles data while trying to keep most of the accuracy and predictive power of the first-principles approach. Although it is becoming very popular in many fields, this concept has been pioneered (38) and extensively used within the ferroelectric community.

We notice that fitting a traditional LGD model on first-principles data is also a kind of second-principles approach. Although these models lack atomic resolution, they provide insightful description of structural phase transitions at a more macroscopic level. These models will not be further addressed here but have been successfully applied to various perovskites (154, 155; see also a review in 156).

3.1. Effective Hamiltonian Approach

Second-principles study of ferroelectric oxides started simultaneously with their first-principles characterization, and the temperature phase diagram of BaTiO₃ was already computed successfully in 1994 using the so-called effective Hamiltonian (H_{eff}) approach (157), which was a generalization of a scheme originally proposed by Rabe & Joannopoulos for GeTe (38). The H_{eff} method relies on the idea of Cochran (17) that the structural phase transition is driven by one or few unstable (soft) modes condensing into the structure; then the H_{eff} method makes use of the microscopic concept of local mode introduced by Lines (21). The local mode ξ_i is a local cooperative pattern of atomic distortion associated to each unit cell i . It can be arbitrarily defined from the soft-mode eigendisplacement vector or, more rigorously, built as the lattice Wannier function (LWF; see **Figure 3b**) related to the phonon branch associated with the relevant unstable mode (158). The Born–Oppenheimer energy surface is then parameterized as a low-order Taylor expansion within the restricted subspace defined by the local modes ξ_i (lattice part) and macroscopic strains η_j (elastic part, which is also coupled to the lattice). The method explicitly treats the LR dipole–dipole interactions and is restricted to local anharmonic terms. All parameters are directly fitted on DFT data and the model used in classical (157) or even quantum (159, 160) Monte Carlo or molecular-dynamics simulations.

Initially designed for bulk ferroelectrics [BaTiO₃ (157, 161), PbTiO₃ (162), KNbO₃ (163), NaNbO₃ (164, 165)], H_{eff} was generalized to address antiferrodistortive (AFD) phase transitions related to rotations of the oxygen octahedra generic to many perovskites [for instance, a quantum paraelectric like SrTiO₃ (159, 166)] or a prototypical multiferroic like BiFeO₃ (167). It was also used to study solid solutions [Pb(Zr,Ti)O₃ or PZT (168, 169), Pb(Mg,Nb)O₃ or PMN (170), Ba(Zr,Ti)O₃ or BZT (171)], SLs (172, 173), and various nano-objects such as nanodots, nanorods, and nanowires (174, 175).

H_{eff} can be used to study the temperature–pressure phase diagram of various compounds, questioning the displacive or order–disorder nature of the phase transitions (161, 176). It was also used to investigate the role of epitaxial strain (177). Furthermore, the method not only provides access to temperature phase diagrams but also allows determination of the temperature evolution of the lattice contribution to functional properties like the dielectric (178), piezoelectric (179), flexoelectric (180), or even electro-optic coefficients (181). It has also been used to correlate chemical and polar orders in relaxors (182) and quantify the electrocaloric effect (183, 184) and is also opening the perspective of achieving properties by design, using the reverse Monte Carlo method (185).

In practice, the phase transition temperatures T_c are systematically and significantly underestimated using H_{eff} , but good qualitative description of the systems can be achieved when rescaling T_c on experimental data. When fitting on LDA first-principles data, part of the underestimate of the ferroelectric T_c was assigned to the systematic volume underestimate of the approximate functional and can be corrected applying a systematic negative pressure. Fitting on first-principles

data obtained with the SCAN functional provides an improvement (145). But, other sources of errors have been evoked, like the restriction to a limited subspace and inaccurate description of the thermal expansion (139).

Being limited to a restricted subspace of relevant degrees of freedom, the H_{eff} method presents the asset of being physically transparent, but at the same time it appears limited to rather simple cases. On one hand, systems presenting a ground state combining many independent lattice contributions—such as *Pnma* perovskites combining sizable in-phase and out-of-phase oxygen rotations and antipolar motions or hybrid improper ferroelectrics—require including an increasing number of local modes, which becomes very challenging. Although proofs of concept have been reported regarding complicated cases like NaNbO_3 (165) or hybrid improper ferroelectrics (186), no successful H_{eff} has been produced yet regarding a prototypical *Pnma* system like CaTiO_3 . On the other hand, systems showing distinct instabilities (like PbTiO_3) in their high-symmetry phase would require the inclusion of all of them even if only one is condensing, because the competition with the latent instability can strongly affect T_c (140) and the latter can eventually appear in some circumstances (187). Accurate estimation of domain-wall (DW) energy also requires including additional degrees of freedom. This motivates the development of all-atoms models.

3.2. Effective Atomic Potentials

Although we refer to them globally here as effective atomic potentials, different approaches have been considered to describe the full lattice dynamics of ferroelectric perovskites from second principles.

A first possible approach consists of the use of historical shell models, in which ions are modeled as massive cores and massless surrounding electronic shells, linked together through springs (188). When adapted to ferroelectric oxides, an anisotropic and anharmonic core-shell interaction must be considered for O^{2-} ions in order to account for the large anisotropic polarizability of oxygen produced by variations of the Ti–O distance (22, 23). In this scheme, interaction between atoms is represented by Coulombic interactions and pairwise potentials that account for the effects of the exchange repulsion together with the van der Waals attraction between atoms. Model parameters—charges, SR potentials, and core-shell interactions—can then be fitted on first-principles data, including energies, forces, phonon frequencies, and eigenvectors, as well as Z^* . Successful models have been obtained for BaTiO_3 (189, 190), PbTiO_3 (191, 192), KNbO_3 and KTaO_3 (193), or even PZT (194) or PMN (195, 196).

Another classical method consists of the popular bond-valence model (197), which relies on the idea that each atom in a crystal structure prefers to realize a certain atomic valence. The actual atomic valence of a given atom is obtained by summing over the bond-valences of this atom with its neighbors, which can be calculated from an empirical inverse power law between bond valence and bond length. Here, the parameters of the model can also be optimized to match a database of DFT structural energy differences and atomic forces, and models have been reported for PbTiO_3 (198, 199), BaTiO_3 (200), or even BiFeO_3 (201).

In 2013, the construction of effective atomic potentials generalizing the original H_{eff} approach was proposed (140). The method is formulated in the basis of individual atomic displacements (i.e., no longer using LWF) and consists of a Taylor expansion of the Born–Oppenheimer energy around the reference paraelectric phase, up to a given order and in terms of atomic displacements and strains, using symmetry adapted terms. As for H_{eff} , the method includes lattice, strain, and coupling terms at both harmonic and anharmonic levels and treats the long-range dipolar interactions explicitly, whereas SR forces are limited to a specified range. The model parameters corresponding to energy derivatives relate to physical quantities that can be calculated directly

from first principles; so, they do not necessarily need to be fitted but can be determined keeping first-principles accuracy. In this context, the database of second-order derivatives as accessible from DFPT (see **Table 1**) already constitutes the full set of harmonic second-principles model parameters, whereas only anharmonic terms need to be fitted on an appropriate training set of first-principles distorted configurations. Of course, the generic energy expansion contains a huge number of terms and related parameters. An efficient scheme for selecting the most relevant terms and fitting related parameters has been proposed in Reference 202. In practice, only anharmonic or eventually both harmonic and anharmonic terms can be fitted together. Successful models have been obtained for PbTiO_3 , SrTiO_3 (140), CaTiO_3 (203), and even $\text{PbTiO}_3/\text{SrTiO}_3$ SLs (204).

The Born–Oppenheimer surface of perovskites typically contains a lot of local minima related to numerous competing phases so that, whatever the type of model chosen (core–shell, bond–valence, Taylor expansion), a very delicate part of the construction consists of identifying a representative training set on which to fit the parameters. Such a training set can be a set of configurations explored during first-principles molecular-dynamics simulations (198, 202), or it can be built considering various potential local extrema of the energy landscape and some paths between them (199) as well as adding some random noise (190).

Models were built on first-principles data using either the LDA or PBEsol-GGA. As for H_{eff} , the correct sequence of phase transitions is typically reproduced, but the transition temperatures are underestimated. Going further, such models were particularly successful for accessing properties inaccessible from first-principles simulations. They were used to compute intrinsic DW motions in PbTiO_3 from a multiscale approach (205), to explore the DW and negative capacitance in $\text{PbTiO}_3/\text{SrTiO}_3$ SLs (204) or to predict the existence of polar skyrmions (206), which has been further confirmed experimentally (207).

3.3. Discussion and Perspectives

Second-principles effective atomic potentials, effective Hamiltonians, and Landau models can be seen as a continuous series of tools for addressing the ferroelectric properties while either including all the structural degrees of freedom or restricting them progressively to the subspace associated with the phonon branch of the soft mode or ultimately to the soft mode itself (see **Figure 3b**). All approaches remain valuable and can be combined to identify the most relevant physics.

Although the initial motivation of second-principles lattice models was to get rid of the electronic degrees of freedom, treating the latter only implicitly might be a limitation in some cases like for studying conductive DWs, looking at photoexcitation of carriers, or studying polaron formation under charge doping. More broadly, for systems showing distinct spin, charge, or orbital orderings, the construction of lattice models becomes very challenging because each ordered state has its own Born–Oppenheimer energy surface and the system can jump from one to another depending on the structural parameters. Some attempts have been reported regarding the construction of lattice and spin H_{eff} for BiFeO_3 (208, 209). Recently, a method has also been proposed to reintroduce explicit treatment of the most relevant electronic degrees of freedom (i.e., those close to the bandgap) in the form of a tight-binding model, while avoiding double-counting with the effective atomic potentials (210). Beyond the field of ferroelectrics and multiferroics, this last method might also be particularly attractive for studying metal–insulator transitions in nickelate and manganite perovskites.

Amazingly, though first-principles modeling has known a revolution over the past three decades, evolving from a variety of specialized home-made codes in the early 1990s to a few robust, integrated, and powerful packages nowadays, no similar evolution has been seen at the second-principles level. Except for the FERAM software package (211) for the construction of H_{eff}

restricted to ferroelectric local mode in simple cubic perovskites, no large-scale tool has been made available yet regarding the automatic construction of second-principles H_{eff} , shell models, or the bond–valence model. This explains why such investigations have remained relatively marginal and restricted to relatively few systems. The recent SCALE-UP (210) and MULTIBINIT (103) initiatives try to take advantage of the expertise acquired at the first-principles level in order to provide well-integrated packages for (semi-)automatic construction and use of second-principles models for systems of any symmetry, eventually combining different types of degrees of freedom (lattice, spin, electrons). Other similar initiatives are also emerging such as LINVARIANT (212).

Second-principles lattice models are becoming relevant to many other fields than ferroelectrics, and various alternative approaches are currently under development (213–217). To date, those presented here are the most robust for reproducing the subtle energy landscape and very complex phase diagrams and diverse behaviors of ferroelectric perovskites.

4. FERROELECTRIC OXIDE PEROVSKITES

Prototypical ferroelectrics like BaTiO_3 or PbTiO_3 belong to the broad family of ABO_3 perovskites (typically, although not always, with a transition metal at the B site). These compounds share at high temperature the same aristotype centrosymmetric cubic phase and are prone during cooling to develop two main kinds of structural distortions: (a) (anti-)polar motions of A and B cations against the oxygens and (b) AFD rotations of their oxygen octahedra (see **Figure 4a**). Following a seminal idea from Pauling (219), these structural distortions can be seen as a way to improve atomic coordination. Their appearance is therefore intuitively linked to relative atomic sizes (r_i) and has been empirically rationalized from the Goldschmidt tolerance factor (220): $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$. A fully compact and stable cubic structure would require $t = 1$. When $t > 1$, the B cation is comparably too small and the compound prone to B-type polar distortion, whereas for $t < 1$, it is the A cation that is comparably too small and the compound prone to A-type polar distortion and AFD oxygen rotations. First-principles simulations were particularly insightful for rationalizing the emergence of a ferroelectric ground state in ABO_3 perovskites and related compounds, revealing sometimes unexpected mechanisms.

4.1. Ferroelectricity in All Its Forms

By definition, all ferroelectric compounds exhibit a switchable spontaneous polarization, $\mathbf{P}$. However, contrary to common belief, the origin of the latter is not necessarily the same in all compounds. Distinct microscopic mechanisms can be at play and each of them can be responsible for specific properties. Identifying which mechanism is responsible for $\mathbf{P}$ in each compound is therefore of primary importance because it helps to rationalize and anticipate why different ferroelectrics can eventually show different properties, as further exemplified in the next sections.

4.1.1. Proper ferroelectricity. Regular ferroelectrics, like BaTiO_3 , are classified as proper ferroelectrics (see **Figure 4b**): They exhibit, in their paraelectric phase, an unstable polar phonon mode ξ (with imaginary frequency ω) that is the fingerprint of a negative energy curvature ($\omega^2 < 0$) related to a double-well energy surface ($E \propto \omega^2 \xi^2 + \beta^2 \xi^4$) and constitutes the primary order parameter of the ferroelectric transition ($\mathbf{P} \propto \xi$). Systematic first-principles computation of the phonons in the high-symmetry structure is therefore a primer tool to identify potential ferroelectric instabilities and is nowadays exploited in the high-throughput search of new ferroelectrics (130, 250).

It quickly appeared from first principles that most ABO_3 perovskites exhibit a polar instability (221) so that a natural question emerged: Why are there finally so few (ABO_3) ferroelectrics? (222).

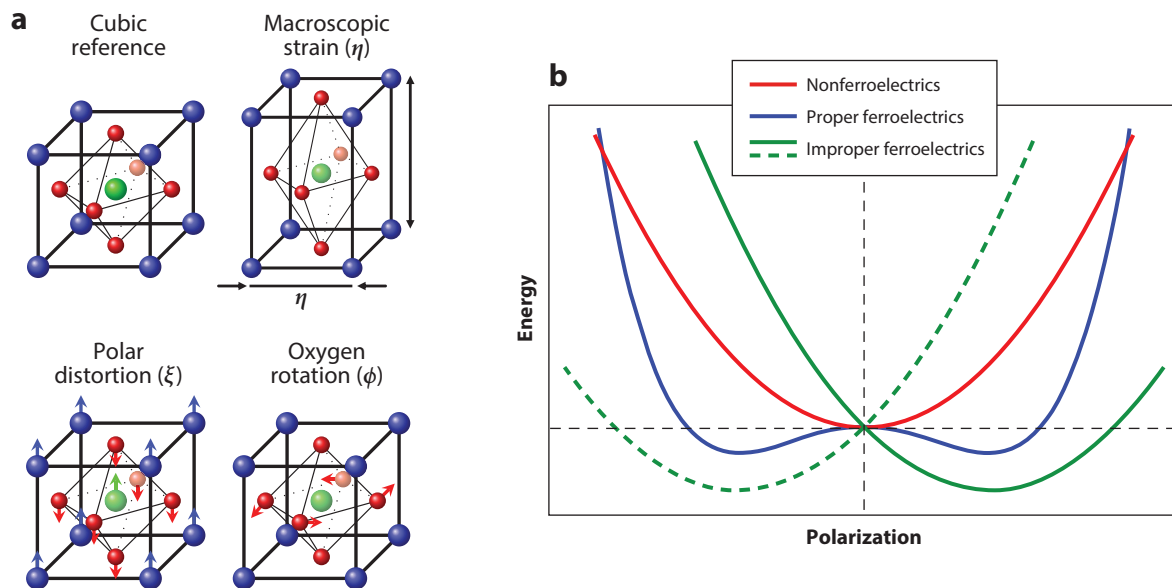


Figure 4

(a) Sketch of the reference cubic perovskite structure and of dominant structural distortions: macroscopic strain (η), polar distortion (ξ), and antiferrodistortive oxygen rotation (ϕ). (b) Typical energy versus polarization curves related to different types of ferroelectrics. Nonferroelectric systems are associated with a single well (red curve), whereas proper ferroelectrics are associated to a double well (blue curve). In improper ferroelectrics, the system is not intrinsically ferroelectric (single well, red), but the linear coupling of $\mathbf{P} \propto \xi$ with the primary order parameter ($E \propto \lambda \phi^n \xi$) shifts the well to lower energy, thus inducing a polarization (from red to green curve). In this case, switching the polarization also requires switching the primary order parameter (from green to dashed green curve). In triggered ferroelectrics, the system is not intrinsically ferroelectric either (single well, red), but the quadratic coupling of $\mathbf{P}$ with the primary order parameter ($E \propto \alpha \phi^2 \xi^2$) renormalizes the curvature at the origin to destabilize $\mathbf{P}$ (from red to blue curve). Strain engineering of ferroelectricity consists of exploiting polarization strain coupling ($E \propto g \eta \xi^2$) to renormalize the curvature of the polarization well thanks to the epitaxial strain (from red to blue curve). Panel b reproduced with permission from Reference 218; copyright 2011 Springer Nature.

In fact, a polar unstable mode ξ is not enough to guarantee a ferroelectric ground state, because independent AFD oxygen octahedra rotation ϕ can be unstable and yield energetically competing phases. The latter are absent when $t > 1$, but they typically lower the energy by a greater margin than ξ when $t < 1$. Furthermore, ξ and ϕ usually compete at their lowest bi-quadratic coupling order ($E \propto \alpha \xi^2 \phi^2$, with $\alpha > 0$), so that they tend to exclude each other (223). As a result, most perovskites with $t < 0$ prefer a nonpolar $Pnma$ ground state combining in-phase and out-of-phase AFD oxygen rotations. The latter phase is nevertheless often in competition with a polar $R3c$ combining out-of-phase oxygen rotations and polar distortion. In this context, the appearance of additional antipolar motions, compatible by symmetry with the coexistence of in-phase and out-of-phase rotations, was shown to play a key role in stabilizing the $Pnma$ phase (222). Although most perovskites are thus not ferroelectric, the polar instability remains latent and can emerge if competing AFD oxygen rotations are suppressed (224, 225). Careful investigation of the energy landscape and of its evolution with external constraints can become tedious at the first-principles level but is also now accessible using second-principles techniques.

Beyond exploring and rationalizing the energy landscape of perovskites, first-principles calculations are also insightful for understanding the microscopic mechanism of the instability. Although ABO_3 perovskites can be classified as dominantly ionic compounds, it was already highlighted by Cohen (42) that partial hybridization between O-2p and B-d states plays a key role. This

can weaken SR forces, and the mixed ionic–covalent nature of the bonding was also shown to be at the origin of anomalously large Born effective charges (Z^* ; 94). In turn, these anomalous Z^* are compatible with a large destabilizing LR Coulombic interaction that can explain the ferroelectric instability (226) in line with Cochran’s picture (16, 17). Independently, chemists sometimes formulated the ferroelectric instability in terms of a pseudo Jahn–Teller (227) instability, suggesting a more local and electronic effect. These formulations are not necessarily antagonists because structural instabilities always ultimately result from electron interactions, and dynamical changes of hybridizations are underlying both views. The previous discussion commonly applies to compounds with $t > 1$ in which the ferroelectricity is dominated by B-type motions. In the case of $t < 1$, the ferroelectricity is more related to the A-type motion, and it appears less directly related to change of hybridizations, although not excluding it, but is more in line with steric effects. In Pb and Bi compounds, the lone pair was also shown to play an active role, highlighting that the origin of ferroelectricity is certainly not unique and that distinct mechanisms can eventually cooperate.

Inspection of the full phonon dispersion curves (41) and related IFCs in real space point out an eventually more insightful classification into what we refer to hereafter as long-range ferroelectrics (LR-FE) and short-range ferroelectrics (SR-FE). In some cases (LR-FE), the ferroelectric instability is confined in some parts of the Brillouin zone around Γ , highlighting the need for relatively LR atomic correlations in real space for the instability to appear. This is typically the case for B-type ferroelectrics ($t > 1$; e.g., BaTiO_3 or KNbO_3) and in line with Cochran’s picture, relying on a competition between SR and LR forces. In other cases (SR-FE), the region of instability appears much more delocalized in reciprocal space, highlighting a geometric or electronic instability more local in real space. This is more the case in A-type ferroelectrics ($t < 1$; lone pair). We discuss in the following sections that such a distinction between LR-FE and SR-FE, directly apparent from the phonon dispersion curves, can reveal useful information for rationalizing distinct behaviors.

4.1.2. Improper and hybrid improper ferroelectricity. Beyond proper ferroelectrics, some other compounds are classified as improper ferroelectrics (228): These do not show any unstable polar mode ξ in their paraelectric phase (single polar well with positive curvature) but instead a nonpolar instability ϕ , which acts as the primary order parameter. Improper ferroelectrics are materials in which ξ couples at linear order with ϕ ($E \propto \lambda \phi^n \xi$, n being the faintness; 229), so that the appearance of ϕ will induce ξ as a secondary order parameter by shifting down the polar well (see **Figure 4b**). A prototypical example is YMnO_3 adopting a hexagonal structure (230). Another one is BaMnO_3 (231). Specific features of improper ferroelectrics are that they do not show polar mode softening around T_c (i.e., no divergence of the dielectric properties; 228) and remain ferroelectric under open circuit (less sensitive to depolarizing issues) (232). We notice that the primary order parameter does not necessarily need to be a structural degree of freedom but can be an electronic one like in TbMnO_3 , where it is the spin magnetic order that induces ferroelectricity (233).

Another class of ferroelectrics are so-called hybrid improper ferroelectrics: These are special cases of improper ferroelectrics in which the polar mode is driven not by one but by two nonpolar modes, ϕ_1 and ϕ_2 , of distinct symmetries through a trilinear term of the form $E \propto \lambda \phi_1 \phi_2 \xi$. Initially revealed in artificial $\text{PbTiO}_3/\text{SrTiO}_3$ SLs (50), this mechanism is quite generic in naturally and artificially layered perovskites (234–238) and can even exist in some phases of simple bulk perovskites (239, 240). Although the origin of ferroelectricity is more indirect, different types of predicted hybrid improper ferroelectric were shown experimentally to be practically switchable ferroelectrics (50, 241).

One peculiarity of (hybrid) improper ferroelectrics is that the polar well remains a single well, and that switching **P** necessarily requires switching also (one of) the primary order parameter(s) ϕ

(see **Figure 4b**). On one hand, this means that they can be eventually more difficult to switch and that they can also give rise to unusual domain structures (241). On the other hand, they include an unusually robust link between distinct degrees of freedom. This is particularly true for hybrid improper ferroelectrics that couple $\mathbf{P}$ with two other modes at linear order. If these modes are linked to independent properties (spin, orbital, or charge orderings), this provides a robust pathway to realize multifunctionalities like electric control of the magnetization (218, 234) or even of Jahn–Teller distortions (240, 242, 243; see Section 4.3.3).

4.1.3. Triggered ferroelectricity. As proposed by Holakovský (244), another potential class of ferroelectrics are triggered ferroelectrics: As for improper cases, the polar mode ξ is not initially unstable, but this time it is triggered by a coupling at quadratic order with the nonpolar primary order parameter ϕ ($E \propto \alpha \phi^2 \xi^2$, with $\alpha < 0$), the appearance of which renormalizes the curvature of the ξ well from positive to negative, thus inducing the ferroelectric instability (see **Figure 4b**). Although this mechanism was suggested for more complex systems, it was not directly reported for any ABO₃ perovskites. This is linked to the fact that the alternative AFD oxygen rotation phonon instabilities typically compete with the polarization (i.e., $\alpha > 0$ as highlighted above). Although this competition looks rather generic, it was shown to be restricted to small rotation amplitudes (223). At larger rotation amplitudes (245), the trend is reversed owing to a higher-order interaction ($E \propto \beta \phi^4 \xi^2$ with $\beta < 0$), so that large rotations can induce a polarization through a mechanism better seen as a steric effect making these compounds SR-FE. This can explain, for instance, why compounds with a very small tolerance factor that crystallize in the trigonal LiNbO₃ structure are also ferroelectric: Their paraelectric $R\bar{3}c$ phase can be seen as a cubic perovskite with very large inherent $a^-a^-a^-$ oxygen rotations that promote the ferroelectric instability (eventually present already in the related cubic phase) instead of suppressing it. As such, they can be seen as a kind of triggered ferroelectric perovskite, although at a higher-order of coupling [$E \propto \alpha' \phi^2 \xi^2$, with $\alpha' = (\alpha + \beta \phi^2) < 0$].

4.1.4. Hyperferroelectricity. A last concept is that of hyperferroelectricity (246). Usual proper ferroelectrics like BaTiO₃ or PbTiO₃ cannot sustain a polarization normal to a surface if the depolarizing field is unscreened. Hyperferroelectricity refers to a class of proper ferroelectrics that remain polar under open-circuit boundary conditions. This condition translates into an unstable LO mode on top of the conventional TO instability and was first revealed in ABC ferroelectric semiconductors. However, an unstable LO mode had been previously identified in LiNbO₃ (247), and it has been shown recently that isostructural LiNbO₃ compounds are typically hyperferroelectrics (248). The hyperferroelectric behavior of LiNbO₃ was linked to the A-type Li motion (249), and it is worth noticing that the eigenvector of the unstable mode evolves from more B-type to more A-type while going from TO to LO configuration (247). A new class of anti-Ruddlesden–Popper perovskites has recently been identified as hyperferroelectrics (250), and many other ferroelectrics could be as well. As a guiding rule, SR ferroelectrics showing (almost) vanishing on-site IFCs and a local ferroelectric character in real space are good candidates for hyperferroelectricity (249). We suggest finally that because they remain ferroelectric under open-circuit boundary conditions, (hybrid) improper ferroelectrics might be classified also by extension as hyperferroelectrics (although without LO nor even TO polar instability).

4.2. Strain Coupling, Piezoelectricity, and Electrostriction

In cubic perovskites, the ferroelectric phase transition does not only arise from the condensation of a polar atomic distortion (ξ) but also is accompanied by the appearance of a macroscopic strain (η). In fact, the strain does not spontaneously appear but is driven by the polar mode through

a coupling term in the energy of the form $E \propto g \eta \xi^2$. As such, proper ferroelectric perovskites can be seen as improper ferroelastics. This polarization strain coupling is at the origin of the piezoelectric properties of the polar phases. More broadly, it also reflects a strong sensitivity of ferroelectricity to mechanical boundary conditions. On one hand, ferroelectricity is known to be quickly suppressed under hydrostatic pressure in perovskites, although it was revealed that it can eventually reappear at very high pressure (251, 252). On the other hand, the strain coupling is at the origin of epitaxial strain engineering of the ferroelectric properties in thin films and SLs, as further discussed in Section 4.3.

First-principles calculations have been successful not only in accessing the intrinsic piezoelectric properties of given perovskites and solid solutions at zero Kelvin but also in exploring their temperature evolution from second-principles models. Two main breakthroughs arose in 2000. First, pioneering finite-polarization first-principles calculations by Fu & Cohen (86) related the giant piezoelectric response of relaxors to the ease with which $\mathbf{P}$ can rotate from one direction to another in an electric field, rather than to a strong modification of the amplitude of $\mathbf{P}$. Exemplifying that on BaTiO_3 , they were implicitly linking giant strain responses to the intrinsic shape of the energy landscape rather than to any other feature of relaxors. Second, accessing finite-temperature properties from a second-principles H_{eff} approach, Bellaiche, García & Vanderbilt (168) confirmed the existence of the recently discovered (253) monoclinic phase bridging rhombohedral and tetragonal phases at the morphotropic phase boundary of PZT. This phase is providing a continuous path for the polarization to rotate from [001] to [111] directions. They further confirmed that the large so-called $d_{33\text{r}}$ piezoelectric coefficient observed in ceramics is in fact coming from a large enhancement of d_{15} , which is also consistent with experimental findings (254). Such a bridging monoclinic phase was further observed in pure PbTiO_3 under pressure (255), highlighting again the generality of the concept. Independently, second-principles calculations also clarified the relationship between cation ordering and polar nanoregions in relaxors (182, 256, 257) and further appeared to be a potential tool for designing optimized piezoelectrics (172). Recent interest is in the search of lead-free piezoelectrics like $(\text{Ba,Ca})(\text{Ti,Zr})\text{O}_3$ (258, 259). We redirect interested readers to more focused reviews on piezoelectrics for more complete overviews (260–262).

Compared with piezoelectricity, other strain-related responses like flexoelectricity or the electrostrictive effect (i.e., the homogeneous strain response to an electric field but at quadratic order in the field) have received much less attention, although they are more generic effects that are also present in centrosymmetric systems. The theory of flexoelectricity is still under development, and calculations are restricted to prototypical examples. Electrostrictive coefficients are, for instance, accessible from finite- $\mathbf{D}$ calculations (263), but at this stage a complete discussion of the electrostrictive effect and its temperature behavior is still lacking.

4.3. Thin Films, Superlattices, and Naturally Layered Systems

Being a collective phenomenon, ferroelectricity is expected to be affected by finite-size effects. From LGD calculations (264), it was initially expected that ferroelectrics is progressively suppressed in thin films. However, as the quality of oxide films was improving, ferroelectricity started to be observed at ultrasmall thicknesses (265), questioning more deeply in the early 2000s the potential existence of a ferroelectric critical thickness. Nowadays, it is understood that there is no unique answer to that question since ferroelectricity is strongly dependent on the imposed boundary conditions (266, 267). Clarifying this issue has not only opened the door to nanoscale applications of ferroelectrics but further boosted the discovery of new strategies to induce it.

4.3.1. Mechanical boundary conditions. Over the past 25 years, tremendous experimental advances have been realized in the growth of oxide thin films, providing access to fully coherent

perovskite oxide films and heterostructures epitaxially grown on a substrate, with high quality-control at the atomic scale (268, 269). In such epitaxial structures, the oxide layers experience mixed mechanical boundary conditions: They adopt the same in-plane symmetry and lattice constants as the substrate (fixed in-plane strains) while they are free to relax out-of-plane (fixed out-of-plane zero-stress).

As already highlighted in the 1950s (270) and previously discussed in Section 4.2, cubic perovskites show a polarization-strain coupling of the form $E \propto g \eta \xi^2$ so that such epitaxial in-plane strains will renormalize the polar mode energy curvature (see **Figure 4b**). Amazingly, with the lowest-order coupling being linear in η , there is always a way (compressive or tensile) to soften the well and enhance the ferroelectric character. Accessible from an LGD approach (271, 272), strain-temperature phase diagrams of different perovskites have been reported from first principles and second principles (177, 273) that also include domain morphology (274, 275). This has guided the possibility not only to boost ferroelectricity (e.g., BaTiO₃; 276) but also to induce it in nonferroelectric compounds (e.g., SrTiO₃; 277). Quickly, strain engineering of ferroelectric properties has become a generic concept (45, 278, 279), which is amazingly not restricted to perovskites but also applicable to simple rocksalt binary oxides like BaO or EuO (280, 281). At the computational level, DFT studies often neglect the different thermal expansions of films and substrates: This was shown recently to play a key role (282) and should be explicitly included to achieve more quantitative predictions.

Beyond tuning the ferroelectric mode itself, epitaxial strain also affects—often in a different way—other lattice modes competing with it (283), thus providing the opportunity to design a ground state favoring either one or the other (284). Along the same line of thought, hidden ferroelectricity can so reappear in *Pnma* perovskites in which the oxygen tilt pattern has been modified or inhibited (224, 225). In these latter examples, the modification of the tilts does not primarily result from the strain imposed by the substrate but rather from the distinctive tilt pattern of the latter. Such additional tilt pattern engineering resulting from distortion coupling at the interface is another inherent effect of the substrate that plays a key role, but it has been less exhaustively explored than strain engineering. Nowadays the high quality of the films allows coherent preservation of strains of a few percent (up to 2–3 %) over thicknesses up to a few 100 nm. Higher strain values (up to 10%) have even been reported when including buffer layers in SLs (281). We notice that extremely large strains are sometimes reported but in reference to the regular phase. In fact, ABO₃ compounds typically show strongly competitive phases, and the strain imposed by the substrate can simply be seen as a way to stabilize a distinct phase that better fits with the substrate. This is, for instance, the case in BiFeO₃ that, instead of its regular *R3c* phase, adopts under large enough strains a so-called T-phase under compression (285) and another *Pmc*2₁ phase under tension (286). Nowadays, MEMS (MicroElectroMechanical Systems) platforms offer an alternative way to achieve high and tunable uniaxial and biaxial strain states in oxides (287) and might provide new opportunities to explore further the useful concept of strain engineering.

4.3.2. Electrical boundary conditions. In an isolated ferroelectric slab ($\mathbf{D} = 0$), any polarization perpendicular to the surface would give rise to a depolarizing field $\mathbf{E}_d = -\mathbf{P}/\epsilon_0$. In ferroelectric capacitors in close circuit, free carriers within the metallic electrodes are expected to provide efficient screening of $\mathbf{E}_d$. Original LGD models developed to explain the thickness dependence of the coercive field (288, 289) so assumed perfect screening of $\mathbf{E}_d$. Then, relying on the same hypothesis of perfect screening, atomic-scale second-principles calculations using H_{eff} predicted that PbTiO₃ thin films between metallic electrodes in short circuit should remain ferroelectric down to three unit-cell thicknesses (290).

All these works were implicitly assuming the presence of ideal electrodes, in which the screening charge accumulates in a plane of negligible thickness at the electrode–ferroelectric interface and compensates exactly the field produced by $\mathbf{P}$ in the ferroelectric film. In 2003, pioneering first-principles modeling of a realistic nanocapacitor made of a BaTiO_3 thin film between SrRuO_3 electrodes highlighted that, contrary to common wisdom, the field is not exactly zero within ferroelectric films between real electrodes in short circuit due to the finite effective screening length at the metal–ferroelectric interface (49). This was, on one hand, providing a first quantitative estimate of the effective screening length at a realistic interface ($\lambda_{\text{eff}} \approx 0.25 \text{ \AA}$) and, on the other hand, computing explicitly its detrimental effect on the ferroelectric properties.

This first-principles breakthrough brought back to the forefront previous discussions regarding the modification (or even the suppression in monodomain configurations) of the ferroelectric properties in thin films by a residual depolarizing field (291). Soon, the predicted evolution of $\mathbf{P}$ with thickness in ultrathin films was confirmed experimentally (through its link with the tetragonality; 292). These effects were also incorporated in models to describe the thickness dependence of the coercive field (293) or the onset of dielectric dead layers in nanocapacitors (294). A lot of activity was triggered to determine the influence of the nature of the metallic electrodes (295), the electrode–perovskite termination (296) and the interfacial chemical bonding (297), or ionic relaxations in the metal electrode (298, 299) in the effective screening and the stabilization of the ferroelectric phase. This highlighted that λ_{eff} is not only a property of the metal electrode but more globally of the interface and that it can eventually become negative in some particular cases (297).

First-principles calculations, as discussed above, were initially restricted to a monodomain state in which the imperfect screening of $\mathbf{E}_d$ progressively decreases the amplitude of $\mathbf{P}$. Depending on the quality of the screening, the system can alternatively prefer to break into domains to avoid $\mathbf{E}_d$ (300). Addressing this from first principles remains challenging (301). Proper treatment of imperfect screening and related residual $\mathbf{E}_d$ has been included in H_{eff} (44), opening the door to the analysis of various interesting domain structures (302).

Electrical boundary conditions also play a key role in SLs alternating ferroelectric and insulating layers, in which they impose the continuity of $\mathbf{D}$ in the direction perpendicular to the interfaces. In those systems, there is a close competition between the electrostatic energy cost related to polarization mismatch and the balance between internal energy cost and gain for polarizing the layers. This often prevents an out-of-plane polarization in naturally layered perovskites (Ruddlesden–Popper, Aurivillius), although a recent exception has been reported (250). In artificial SLs, the nature and thickness of the insulating layer appeared as a new efficient design parameter through screening engineering. For ultrathin and highly polarizable insulating layer (like SrTiO_3), the system can be homogeneously polarized like in $\text{BaTiO}_3/\text{SrTiO}_3$ (303), offering the possibility to finely tune ferroelectric properties as illustrated in $\text{PbTiO}_3/\text{SrTiO}_3$ (304). Playing with the layer thickness, the system can also break into domains (152), eventually generating exotic structures like skyrmions (206), as further discussed in the next section. In some cases, the ferroelectric layer can evolve to an antipolar configuration (305), offering a pathway to the design of antiferroelectrics (306).

Importantly, the survival of a spontaneous polarization in thin films down to the nanometer scale has opened the possibility to design ferroelectric memory devices that would scale up to ultrahigh densities. In that context, a very appealing concept is that of ferroelectric tunnel junctions (FTJs). The device, historically coined as a polar switch by Esaki et al. in the early seventies (307), consists of two metal electrodes separated by a nanometer-thick insulating ferroelectric barrier through which electrons can tunnel (308). The underlying idea is that the tunnel current (or the electrical resistance) depends on the orientation of the polarization so that its measurement offers

a nondestructive readout of the polarization state. This phenomenon, known as the tunneling electroresistance (TER) effect, is crucial for the development of memory devices that overcome the limitations of conventional semiconductor memory devices based on charge storage owing to their higher density, low operating power, nonvolatility, and nondestructive readout capabilities (309). The concept was first developed in an analytical model by Zhuravlev et al. (310), later confirmed by first-principles simulations (311), and experimentally demonstrated (312, 313). It is often assumed that large TER requires asymmetric FTJs involving two different metallic electrodes (310), but it has been shown to be also intrinsic to FTJs with symmetric electrodes in which the only asymmetry arises from the polarization itself (314). In subsequent works, the combination of FTJs with magnetic tunnel junctions gave rise to multiferroic tunnel junctions (a four-state resistance device; 315), and giant TER effects controlled by spin valves (316). More focused reviews on this topic can be found in References 317 and 318.

Notice that the DFT treatment of metal–ferroelectric interfaces always requires some caution. As previously discussed, the electronic bandgap of insulators is often strongly underestimated in DFT when using (semi-)local functionals. This prevents accurate prediction of Schottky barrier heights and eventually gives rise to pathological situations in which the Fermi level of the metal erroneously aligns with the conduction states of the ferroelectric rather than properly appearing in the gap (266), as sketched in **Figure 2b**. A full review on how to detect the problem and its consequences can be found in Reference 85.

4.3.3. Symmetry breaking. Beyond the mechanical boundary conditions (strain and tilt pattern engineering) and the electrical boundary conditions (screening engineering), another key effect in layered structures is the breaking of symmetry. In some cases, the atomic arrangement can break inversion symmetry by itself. This was shown to be the case, for instance, in tricolor A/B/C SLs (319) that are spontaneously polar. If the symmetry breaking is not too large, the system can remain switchable between two asymmetric minima while eventually showing enhanced polarization (320). This has fueled experimental developments that have confirmed theoretical predictions (321). This also revealed useful in multiferroics (322) and even when combining non-ferroelectric compounds (323). Let us notice that the concept is not restricted to tricolor lattices and that breaking of inversion symmetry is also inherent, for instance, to bicolor 1/1 ABO₃/A'B'O₃ SLs in which $A \neq A'$ and $B \neq B'$.

In many other cases, inversion symmetry is preserved, but the atomic ordering inevitably modifies some of the symmetries and, consequently, the way distinct structural distortions can couple together. A breakthrough arose in 2008 when a new type of improper ferroelectricity was discovered in PbTiO₃/SrTiO₃ artificial SLs (50). This work revealed a new mechanism in which ferroelectricity emerges in the SL from an unexpected trilinear coupling ($E \propto \lambda P \phi_1 \phi_2$) of **P** with two independent nonpolar rotation modes (ϕ_1 and ϕ_2) that is forbidden in bulk perovskites. This mechanism, nowadays referred to as hybrid improper ferroelectricity, quickly appeared more generic than initially thought: It was revealed to be in play in Ca₃Mn₂O₇, a naturally layered Ruddlesden–Popper compound (234) or in NaLaMnWO₆ double perovskites (235); it appeared generic in artificial ABO₃/A'BO₃ SLs combining *Pnma* perovskites (236, 237); and it was even predicted in metal–organic frameworks (242). More than a new way to achieve ferroelectricity, the trilinear coupling of lattice modes also quickly appeared as a promising way to achieve new multifunctional properties. Coupling polarization to oxygen rotations that tune spin orientation was proposed as a promising way to achieve electric switching of the magnetization (218, 234, 324). But the trilinear coupling is not restricted to oxygen rotations; it can also involve other types of atomic motions such as Jahn–Teller distortions and antipolar motions, enlarging the scope of potential multifunctional applications (239, 240, 242, 243, 325). Hybrid improper

ferroelectrics has become a broad field in itself that would be impossible to summarize here (see, for instance, 238). Still, most investigations have been restricted at the first-principles level. Pioneering second-principles simulations have been reported in Reference 186, but questions remain, for instance, regarding the temperature behavior of hybrid improper ferroelectrics and the exact mechanism of their phase transition (326).

4.3.4. Substrates and surfaces. The engineering of the ferroelectric properties in thin films and SLs has required the development of a family of appropriate substrates (45). Nowadays, most works and developments exploit the atomic flexibility of the perovskite structure to provide a wide variety of ABO_3 substrates. This allows cube-on-cube growth of high-quality ferroelectric thin films and SLs with finely tuned multifunctional properties (268, 269, 327).

Another challenge is the direct integration of multifunctional oxides into electronic devices from the epitaxial growth of perovskites directly on silicon (328). Pioneered experimentally by McKee et al. in 1998 (48), this topic has attracted theoretical interest from the early stages (329). Pedagogical overviews regarding first-principles advances can be found in References 330–332. With SrTiO_3 being a very popular substrate for the growth of perovskite films, most of the focus has been on the prototypical Si/SrTiO_3 system that is considered an ideal template for the further growth of other functional perovskites. Part of the interest has focused on the band alignment at the interface in relationship with its atomic structure (333). Another question concerned the possible ferroelectric properties of SrTiO_3 on Si. A priori, the compressive epitaxial strain should make it ferroelectric, but it has been argued that the transfer of charge at the interface and related built-in dipole is pinning the polarization and preventing switching in the regime of thickness in which the film remains under epitaxial constraint (333, 334). Still, this conclusion might depend on the structure of the interface, and ferroelectric switching might eventually be possible in the case of a less ionic interface (335).

The explosion of graphene (336) and related two-dimensional materials has also boosted the efforts to integrate ferroelectrics with these emerging technologies. Relatively few first-principles investigations have been reported to date, but those that exist have shown how the electronic and spin structure of graphene-related materials can be tuned by ferroelectric field effects (337–340). Other ferroelectrics beyond oxides (such as organometallic halide perovskites (341)) compatible with the hexagonal lattice have also been theoretically explored.

Another emerging topic is the use of ferroelectrics for tuning surface reactivity and catalysis. The surfaces of ferroelectrics are strongly dependent on their polarization states so that control of the polarization has been seen as a practical way to tune surface chemistry and catalytic properties. Known since the mid-twentieth century, this concept has recently witnessed renewed interest (342, 343). First, catalysis requires optimal strength of interaction between the molecules with the surface (Sabatier principle) and fine-tuning of the polarization through the pyroelectric or piezoelectric effect can help achieve that goal. Then, ferroelectrics open the door to switchable surface chemistry (344–346): Cycling the surface between distinct polarization states with distinct interaction strengths could drive an appropriate set of reactions by periodically adsorbing and releasing some molecules. Although various proofs of concept have been reported (342), practical implementations of these ideas would require identifying an appropriate range and practical ways to efficiently control the polarization.

4.4. Domain Walls, Domain Motion, and New Topological Structures

A common feature of all ferroelectric crystals is the formation of domain structures when a paraelectric phase is cooled through the ferroelectric transition temperature. These domains are small spatial regions with different polarities separated by a boundary, referred to as the DW. Domains

of opposite polarization lead to overall charge neutrality at the surfaces, reducing the depolarizing field and the associated electrostatic energy.

Pioneering H_{eff} calculations were carried out for 180-deg domains in tetragonal BaTiO_3 (347), and first-principles simulations were done on 180-deg and 90-deg domains in PbTiO_3 (348), unraveling the fully relaxed atomic structure, the DW energy, and the polarization profile across the DW and providing an estimate of the barrier height for DW motion. Second-principles simulations have been also used to demonstrate in ferroelectric (349) and multiferroic (350) thin films down to three unit cells the universality of Kittel's law, stating that the width of ferroelectric domains scales as the square root of the thickness of the film.

DWs have different symmetries than those of the domains and may therefore show distinct properties. Surprising effects can arise such as the onset of an electrical conductivity at the DW of wide-bandgap insulating materials, like BiFeO_3 (351) or $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (352). Here, the atomistic simulations have pointed to some extrinsic effects (presence of defects or oxygen vacancies) as the origin of the charge carriers (353). It was also predicted from second principles that DWs can have their own ferroelectric transition, independent of that of the material itself (354).

DWs are mobile objects whose position and shape can be controlled by an external stimulus. In particular, DW motion is crucial in polarization switching. First investigations, based on the phenomenological LGD theory, assumed that the crystal remains in a macroscopically homogeneous state (without domains) and overcomes the potential energy barrier that separates the two enantiomers. This model predicted a coercive field orders of magnitude larger than the experimental ones. Soon after the discovery of domains, new switching models were developed based on the inhomogeneous domain nucleation and dynamic within the Kolmogorov–Avrami–Ishibashi model (355, 356). Although the second mechanism is the most common one in ferroelectric thin films, the first one was observed in 1998 for the first time in a random copolymer (357), and later in PbTiO_3 epitaxial ultrathin films induced by changing the chemical potential in equilibrium with the film surface (358). Here again, atomistic simulations have been instrumental. The capability of molecular-dynamics simulations to deal with large systems at finite temperature and under external electric field has been used to simulate the movements of 90-deg DWs during switching in PbTiO_3 films (359), enabling the construction of a simple nucleation-and-growth-based analytical model that quantifies the dynamics of many types of DWs in various ferroelectrics. The two switching models seem to appear in different phases of BiFeO_3 (360). The role of the chemical environment to control the polarization orientation in a ferroelectric film has been studied in Reference 361. A comprehensive theory of domain switching in the ferroelectric crystals and films can be found in Reference 362.

Mobility and large polarizability of DWs make them more responsive to applied external fields than the system as a whole (204) and play a crucial role in novel functional properties. A prototypical example is the emergence of regions with a local negative capacitance, which implies a local voltage drop as opposed to the overall applied bias (363).

First- and second-principles simulations have also predicted how the atomic structure of the domains might be far more complex than initially assumed, adopting the shape of flux-closure domains, quadrants, or vortices (152, 301), being nicely confirmed by experimental observations in $\text{PbTiO}_3/\text{SrTiO}_3$ SLs (364; as shown in **Figure 3c**). In all these structures, the polarization rotates continuously to minimize its gradient and avoid the formation of polarization charges. The resulting gain in electrostatic energy overcomes the cost owing to the strong crystalline anisotropy. Those structures resemble the point singularities and topological defects previously found in magnets, or in ferroelectric nanodots, nanowires, and nanorings (174, 175), opening the door for its topological classification in terms of integer topological indices, such as the vorticity (365). Later, effective atomic potentials have predicted nontrivial topological polar

skyrmions in $\text{BaTiO}_3/\text{SrTiO}_3$ nanocomposites (366), in single phase PbTiO_3 (206), or in $\text{PbTiO}_3/\text{SrTiO}_3$ SLs (207). These novel phases host exciting properties, such as chirality (367), negative capacitance (368), or a huge tunability of the dielectric constant with the external field (369).

First- and second-principles simulations have contributed to unraveling the origin of such complex whirling polarization textures. For Pb-based compounds, it can be traced back to the fact that the common 180-deg domain walls in PbTiO_3 have a Bloch-like character at low temperature, with a spontaneous electric polarization confined within the DW plane (354). This contrasts with the case of the magnetic topological structures, where the Dzyaloshinskii–Moriya interaction (DMI) plays a major role in the stabilization. Indeed, no electric counterpart was known till very recently, when Zhao and coworkers (370) proved that it exists in perovskites, with a one-to-one correspondence with the magnetic situation. The strength and coupling of the electric DMI is mediated by oxygen octahedral tilting and rotations, which couple in a trilinear form with ferroelectric or antiferroelectric motions for the A and B cations, and mimics the spin–orbit coupling in magnetism.

Certainly, the physics behind the DWs and related phenomena is so broad that it is impossible to cover it within the limits of the present review. We redirect the reader to more specialized reviews, like the one by Catalan et al. (371).

4.5. Magnetoelectric Multiferroics

The interest of the ferroelectric DFT community for magnetoelectric multiferroics combining ferroelectric and (anti-)ferromagnetic orders likely started because of the provocative question of N. Spaldin: “Why Are There So Few Magnetic Ferroelectrics?” (372). Focusing on ABO_3 perovskites with a transition metal at the B site, the argument was that ferroelectricity in these systems, as previously suggested by Matthias (373), typically requires d^0 -ness, whereas magnetism requires instead partial occupancy of the d states. In fact, such a d^0 -ness is in line with prototypical Cochran-type ferroelectrics such as BaTiO_3 in which ferroelectricity is related to B- d -O-2p hybridizations, but as previously discussed, various mechanisms can give rise to ferroelectricity, so over the years, d^0 -ness appeared not to be a strict requirement for ferroelectricity. Ferroelectricity can be driven at the A-site like in BiFeO_3 (374), which has become the prototypical example of room-temperature multiferroics (375). It can also survive at the B-site like in strained CaMnO_3 (284). It can also be induced through improper coupling either with another lattice mode like in YMnO_3 (230) or even with the spin order like in TbMnO_3 (233), or it can result from hybrid improper ferroelectricity (234, 324). Hyperferroelectrics, in which the ferroelectricity is SR and more geometric, are also prone to stay ferroelectric (and to become multiferroic) when the active atoms become magnetic (250), and this might be a guiding rule to be further exploited. Ferroelectricity can moreover be engineered by strain in magnetic systems and SLs providing numerous alternative routes (269, 281, 376) to realize multiferroics. Since 2000, magnetoelectric multiferroics have generated an interest that became eventually broader than that for simple ferroelectrics! It is impossible to address this topic more broadly here, but we refer readers interested in multiferroics to other reviews (377–381).

4.6. Doped Ferroelectrics and Ferroelectric Metals

Usual ferroelectric perovskites are typically wide bandgap semiconductors with a negligible number of excited carriers at room temperature. Due to partial off-stoichiometry (e.g., oxygen vacancies), they are however often self-doped, and it is questionable if the presence of charge carriers can affect their properties. Relying again on the seminal idea of Cochran that the

ferroelectric distortion arises from a competition between LR dipolar interactions and SR forces, it was expected to disappear quickly under doping and not to exist in metals.

Relatively fast suppression of ferroelectricity over doping has been confirmed from first-principles calculations for BaTiO_3 (382), which obeys Cochran's picture. Beyond quantum fluctuations, doping could also partially explain why SrTiO_3 , often naturally *n*-doped, is not ferroelectric at low temperature. The fact that ferroelectric materials can survive to some screening in robust ferroelectrics was discussed in terms of metascreening (383) and also related to covalency effects (384). As previously discussed, there are also distinct mechanisms for ferroelectricity. In case the compound behaves as an SR-FE—like in A-type ferroelectrics—the ferroelectric instability appears much more robust over doping and can even survive at large doping (385, 386). The case of PbTiO_3 that combines SR-FE at the A site (lone pair) and LR-FE at the B-site (Cochran type) is illustrative: It remains ferroelectric over substantial electron doping but the ferroelectric distortion evolves progressively to a more A-type character. The fact that B-type ferroelectricity is more sensitive to doping than A-type can be related to its longer-range character involving dipolar interactions but also to the fact that doping electrons are populating the B-*d* states while not affecting the electronic environment at the A site. Hyperferroelectrics, in which ferroelectricity is more local and less sensitive to depolarizing issues, are expected to be more robust over doping. The same is true for improper ferroelectrics (383).

Together with the evolution of the ferroelectric properties, it must be pointed out that strain relaxations are often done in previous first-principles studies, eventually highlighting a large strain effect over doping (382, 383, 387). However, such a result must be taken with extreme care because, at the technical level, volume relaxation cannot be naïvely done with charge doping in practical implementations in which the added charge is compensated by an opposite background (388, 389). This is illustrated in **Figure 2c** showing that computed pressure is ill defined under doping and can change drastically from one code to another depending on the convention chosen for the energy reference. It is worth noticing also that the extra charges are treated as free carriers in those studies, whereas these compounds are prone to develop polarons; modeling the latter remains challenging at the first-principles level but has recently become accessible to second principles.

These concepts have also been considered for designing so-called ferroelectric metals (390), which preserve a ferroelectric-like distortion while being metallic. Such compounds are not regular ferroelectrics since **P** is ill defined in metals (67), but they adopt a polar space group and can eventually be switched by an external electric field (391) or a strain gradient (392). As for **P**, defining Z^* is problematic in metals but it has recently been shown that nonadiabatic Z^* can be defined, and this might help to quantify the lattice distortion (393). The symmetry breaking in metals is appealing for inducing asymmetric transport (394) or even potentially improving the screening (395). Again, survival of the ferroelectric distortion in a metal appears paradoxical when relying on Cochran's picture (LR-FE) but remains much more plausible for compounds belonging to families of SR-FE like in the case of LiOsO_3 (391, 396). So, families of ferroelectrics robust over doping (A-type, hyperferroelectrics) appear suitable for discovering new ferroelectric metals (397). In a similar spirit, hybrid improper ferroelectricity appears to be another path for designing new ferroelectric metals (394). Polar metals were also designed by tilt engineering (224) or by built-in symmetry breaking in tricolor SLs (398). A short review is provided in Reference 386.

4.7. Rashba Ferroelectrics

In nonmagnetic crystals, one can expect the energy bands of up and down spin electrons to be degenerate in the absence of magnetic fields. However, in noncentrosymmetric crystals like ferroelectrics, spin-orbit coupling can lift such a spin band degeneracy through the so-called

Rashba and Dresselhaus effects. Rashba ferroelectrics define a new class of functional materials combining ferroelectricity and Rashba effect and in which the spin-texture related to the Rashba spin-splitting around the band edges can be electrically switched upon reversal of the ferroelectric polarization (399). These materials should (*a*) be a priori nonmagnetic ferroelectric insulators with a sizable switchable polarization and a reasonable bandgap; (*b*) include heavy ions with large spin-orbit coupling and exhibit close to the valence or conduction band edge a significant Rashba spin-splitting that is reversible with the polarization; and (*c*) for applications based on spin and/or charge currents, preserve those properties under appropriate doping. First highlighted in GeTe (400), this concept has been reported also in BiAlO₃ (401) but remains unusual in ABO₃ perovskites. It has been rationalized recently that the conditions for Rashba ferroelectricity are typically not met in simple ABO₃ perovskites with a transition metal at the B site but can be recovered in layered perovskites like Bi₂WO₆ Aurivillius phase (402). The concept of Rashba ferroelectrics has been recently extended to magnetoelectric multiferroics (403).

4.8. Photovoltaics and Photorelated Effects

The photovoltaic effect is the direct conversion of light to electricity. This process to generate a voltage and electric current in a material upon exposure to light consists of two consecutive steps: First, the generation of photocarriers (electron and holes) after excitation by light. Second, an efficient carrier separation (to avoid recombination) and collection at the electrodes. In traditional solar cells, the separation is due to the potential developed at *p-n* junctions. However, there are other mechanisms for separation that do not require sophisticated heterostructures but rely only on bulk properties of single noncentrosymmetric phase materials. This is the case of the shift current, one of the major sources of bulk photovoltaic effects, whose driving force is the coherent evolution of electron and hole wave functions. Ferroelectric materials satisfy the symmetry conditions to hold shift currents. A full theory to compute shift currents from first principles has been developed and applied to PbTiO₃, BaTiO₃ (404), and the multiferroic BiFeO₃ (405). Important conclusions were drawn, such as the generation of open-circuit voltages much larger than the bandgap and the fact that a larger polarization does not always imply a larger shift current response. Large shift currents might also depend on the bonding or antibonding character of the states involved in the transition. A review on the history, development, and recent progress in understanding the mechanisms of bulk photovoltaic effect can be found in Reference 66. Besides these bulk effects, the depolarizing fields that appear in thin films and SLs, or internal fields at DWs (406), could be highly efficient mechanisms for photocharges separation.

Beyond photovoltaics, there is nowadays an increasing interest for photorelated effects, like photostriction (407) or photoinduced ferroelectric phase transition (408). These topics have been addressed at the first-principles level. Emerging second-principles models combining lattice and electrons could open totally new perspectives in this emerging field.

4.9. Electrocalorics

The electrocaloric effect, i.e., the electric-field-induced change in temperature in an insulator, is also a problem under active investigation (409). It is expected to be particularly strong in ferroelectric and antiferroelectric materials because of their anomalously large dielectric responses and the field-driven phase transitions that can be easily induced near the Curie point. This competition between phases is one of the key points to achieve large electrocaloric effects, due to the big entropy shifts produced by the drastic change in the atomic structures. Both direct and indirect methods have been used to estimate the change in temperature under the application of the field (410). The first ones rely on the direct computation of $\Delta T(\mathbf{E})$ under adiabatic conditions.

The second relies on the numerical integration of the Maxwell thermodynamic relations (183). Giant electrocaloric effects have been predicted in alloys (184), ferroelectric nanowires (411), and thin films (412), including multiferroic materials (413). A more complete review on first- and second-principles calculations of the electrocaloric effect can be found in Reference 414.

4.10. Antiferroelectrics

The concept of antiferroelectrics was introduced by Kittel in 1951 (415), in close analogy with magnetism and quickly exemplified in PbZrO_3 (416, 417). At first more a scientific curiosity, antiferroelectrics have recently known a renewed interest in view of potential high-density energy-storage applications.

Although Kittel originally associated the antiferroelectric to material with antipolar alignment of dipoles, antiferroelectrics are more precisely defined in textbooks (229, 418) as antipolar crystals (i.e., that can be described in terms of sublattices with equal but opposite polarization) whose free energy is closely comparable with that of a ferroelectric modification of the same crystal and which may therefore be switched from antipolar to ferroelectric by the application of an external electric field. As such, antiferroelectrics are characterized by a double hysteresis loop that makes them attractive for energy storage.

The concept of antiferroelectrics has been recently reexamined by Rabe (419) and also by Tolédano & Guennou (420). Recent first-principles studies focus, on one hand, on the search for new antiferroelectrics (306, 421) and, on the other hand, on a better understanding of the antiferroelectric behavior of prototypical antiferroelectrics like PbZrO_3 . Investigation of PbZrO_3 from first principles (41, 422) and second-principles (423) dates back to the nineties but without elucidating its complex behavior. Some years ago, it was proposed that the phase transition of PbZrO_3 could be interpreted as a missed incommensurate transition (424). Independently, AFD oxygen rotation and a trilinear mode coupling were pointed out as key ingredients to stabilize the unusual 40-atom *Pham* ground state (425). Going further, K. Shapovalov and M. Stengel (private communication) highlighted very recently the existence of an another essential rototopolar coupling combining polarization, rotation, and rotation gradients. Although this is converging toward a coherent picture, it now appears that the 40-atom *Pham* phase, although experimentally observed, might not be the true ground-state of PbZrO_3 (426, 427). All this reveals a complex and unusual energy landscape with various local minima which might be key for field-induced transition to the polar phase and the emergence of antiferroelectricity.

4.11. Discussion and Perspectives

As highlighted above, many efforts have been devoted over the years to investigate how to finely tune the polar distortion of ferroelectrics not only with an electric field or with temperature but from different means including the coupling with strain, magnetic field, other lattice modes, charge doping, photoexcitation of carriers, etc. Along that line, an emerging avenue consists of the selective excitation of phonons with intense light to access hidden phases. The basic idea is that the incident field drives one particular mode, which might be in the infrared or in the terahertz regime, that then can couple to other mode displacements to stabilize otherwise metastable hidden phases. This technique has been applied to achieve dynamical control of magnetic properties (428, 429). It was also revealed as useful to induce transition toward the hidden ferroelectric phase in quantum paraelectric SrTiO_3 (430) and could also provide ultrafast control of its optical properties (431).

In spite of numerous successes, first-principles and second-principles modeling of perovskite oxides remain limited to relatively ideal structures. An important challenge for the future is certainly to better include and describe different types of defects such as oxygen vacancies (432–435).

This review remains focused on oxide perovskites. However, it is worth noticing that many other ferroelectric materials are generating broad excitement. These include hafnia (436, 437) or 2D ferroelectrics (438, 439) to cite only few. Here too, first-principles modeling is playing a key role and requires facing new challenges (440, 441). Notice finally that the physics of ferroelectrics not only is of interest to the solid state physics and materials science communities but also offers amazing connections to other fields such as cosmology (442), biology (443), or nuclear physics (444).

5. CONCLUSIONS

Although limited to a relatively small community, the first-principles and second-principles modeling of ferroelectric perovskites has not only had a strong impact within the field of ferroelectrics but has more broadly played a key role in the development of condensed matter physics over the past three decades. Retrospectively, the still running series of *Fundamental Physics of Ferroelectrics* workshops, launched by R. E. Cohen in 1990, and the personalities of the people who were involved at the early stages of the field's development have certainly played key roles in this success story! They have contributed not only to building a community but also to creating a real family in which people are working together avoiding sterile competitions and welcoming new ideas with a positive and open mind. Importantly, theorists have also worked hand in hand with experimentalists from the early stages, creating synergies and positive feedbacks. Like in the 1980s, we might think again that, at this stage, everything is known about ferroelectrics! In the 1990s, providing predictive description of properties at the nanoscale, first-principles calculations have revolutionized our understanding of ferroelectricity and related phenomena, taking totally unexpected directions. Today, second-principles simulations open the door to predictive modeling of ferroelectrics at the mesoscale, opening totally new perspectives and most likely a new era in the modeling of ferroelectrics. We hope this review contributes to motivating young people to enter the exciting field of first-principles and second-principles modeling of ferroelectrics, pursuing the work while preserving the same positive and constructive spirit from the early stages that has been the key of the field's success!

SUMMARY POINTS

1. We have provided an overview of the progress realized during the past 30 years regarding the theory and modeling of ferroelectric perovskite oxides and their application in practical systems.
2. First-principles simulations have allowed researchers to make significant advances in the field of ferroelectrics.
3. Reciprocally, the study of ferroelectrics was at the origin of theoretical breakthroughs, with an impact beyond the limit of the ferroelectric community.
4. The advent of second-principles methods allows researchers to overcome the limitation of first-principles simulations in terms of time- and length-scales, paving the way to the atomistic simulation of ferroelectric materials under operative conditions.
5. The continuous synergies and feedbacks between theory and experiment have driven the field to fruitful playgrounds.

FUTURE ISSUES

1. Further progress is needed on density functional theory functionals to increase the accuracy and efficiency of first-principles calculations simultaneously on the structural, electronic, and magnetic properties.
2. The precision and accuracy of second-principles methods must be better assessed in order to evolve toward high-throughput databases and machine learning approaches.
3. Research must go beyond second-principles lattice models and self-consistently couple lattice to spin or electronic degrees of freedom (beyond the proof of concept).
4. Studies must look beyond ideal materials and include different kinds of defects.

DISCLOSURE STATEMENT

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