Many-body and Covalence Effects in the Polarization of Ferroelectric Perovskites

R. Resta$^{(1,2)}$ and S. Sorella$^{(2)}$

(1) Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

(2) Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Beirut 4, I-34014 Trieste, Italy

Abstract

The ferroelectric polarization of perovskite oxides is much larger than implied by displacement of static ionic charges. We use an explicitly correlated scheme to investigate the phenomenon; charge transport is evaluated as a geometric quantum phase. Both covalence and electron-electron interaction enhance polarization in the weakly correlated regime. At higher values of the electron-electron interaction, the system undergoes a transition from a band insulator to a Mott insulator: the static ionic charge is continuous across the transition, whereas the polarization is discontinuous. Above the transition, oxygen transports a positive charge.

SISSA Preprint # 174/94/CM/MB
The large values of the spontaneous polarization in ferroelectric perovskites cannot be explained on the basis of a simple ionic model. For instance, the effective dynamical charge associated to an oxygen displacement during the ferroelectric distortion is of the order of $-6$, i.e. about three times the nominal static value given by a completely ionic picture [1,2] (atomic units of charge are adopted throughout). First-principles calculations, performed within the local-density approximation (LDA), have demonstrated that this effect is due to a large amount of covalence [3]: as a basic feature of such calculations, the effect of electron-electron interaction is accounted for in a mean-field way. In the present paper we investigate a different facet of the problem, namely how the picture is changed by explicitly considering correlated wavefunctions: such investigation is based on a completely different theoretical and computational scheme. In the moderately correlated regime, we find that the electron-electron interaction reduces the static ionic charges but—in apparent contradiction—significantly enhances the macroscopic polarization. At higher values of the electron-electron interaction the system has a transition from a band insulator to a Mott insulator, first investigated by Egami et al. [4]. When we examine the transition from the standpoint of macroscopic polarization, several exotic phenomena show up. In particular the static ionic charges are continuous, whereas the polarization is discontinuous: therefore the polarization (or equivalently the associated geometric quantum phase [5,6]) is the primary order parameter for the transition.

The ferroelectric perovskites have formula unit $\text{ABO}_3$, where A is a mono- or divalent cation, and B is a penta- or tetravalent cation in the transition series. The simplest ferroelectric structure is the tetragonal one, where the most important symmetry-breaking distortion is a relative displacement of the B sublattice with respect to the O one. The essence of the phenomenon can be schematized by considering only the linear O–B chain along the ferroelectric axis, which is symmetric in the paraelectric (so-called prototype) structure, and asymmetric in the ferroelectric one. In order to make a correlated wavefunction available, we schematize the Hamiltonian of such a linear model ferroelectric with a two-band Hubbard model at half filling, first introduced by Egami et al. [4], and whose macroscopic polarization
has not been investigated so far. In order to reduce the number of parameters, we arbitrarily set equal values of the Hubbard $U$ on anion and cation. The Hamiltonian of the prototype structure is therefore

$$\sum_j [ (-1)^j \Delta c^\dagger_{j\sigma} c_{j\sigma} - t_0 (c^\dagger_{j\sigma} c_{j+1\sigma} + \text{H.c.}) ] + U \sum_j n_{j\uparrow} n_{j\downarrow} ,$$

and depends on two parameters besides $U$: the hopping $t_0$, and the difference in site energies $E_B - E_O = 2\Delta$. We restore charge neutrality by assigning a classical charge of +2 to the cationic sites: this ensures that in the extreme ionic limit ($t_0 = 0$ and $U < 2\Delta$) the total static charges are $\pm 2$. The energy difference $E_B - E_O$ is of the order of 3 or 4 eV in the materials of interest, taking e.g. Ti or Nb as the B cation; it also equals the gap of the noninteracting model. In the following of this study we assume $\Delta = 2$ eV, and $t_0 = 3.5$ eV, such as to get a mean-field band width of 5.3 eV, which is a realistic value for the valence bands of these materials. The fact that $t_0$ is of the order of $2\Delta$ clearly indicates a mixed ionic/covalent character.

We plot in Fig.1(a) the static ionic charge as a function of $U$ (triangles). The calculations have been performed in 8-sites supercells, using skew (quasiperiodic) boundary conditions on each electronic variable, and then taking the average over the boundary conditions (alias over the supercell quasimomenta $k$), as in Ref. [8]. This ensures that the $U \to 0$ limit is numerically equal to the fully converged thermodynamic limit of the noninteracting calculation. Typically we have used 30 $k$ points, corresponding to 120 $k$ points in the unfolded Brillouin zone of the noninteracting system. The numerical diagonalization was performed via the well known Lanczos algorithm, which provided the ground state electronic wavefunctions $\Psi_0(k)$ with an energy tolerance close to the machine accuracy ($10^{-12} t_0$), with less than 100 Lanczos iterations in all cases. In order to reduce the problem size we have explicitly used the conservation of the number of spin-up $N_{\uparrow}$ and spin-down $N_{\downarrow}$ particles. The subspace with $N_{\downarrow} = N_{\uparrow} = 4$, where the ground state lies, contains only 4900 elements, thus allowing a large reduction of the full Hilbert space (amounting to $4^8 = 65536$ elements). Use of the center-of-mass translation symmetry is also possible, but becomes useful only for
larger systems. In an insulating system as the present one the size effects are small, and further minimized by \( k \)-averaging \([8]\). For a few parameter values we have indeed performed 12-sites calculations, and checked that the results agree with the 8-sites ones to within one per cent, at least for the quantities studied here.

The ferroelectric distortion is the zone-center optical phonon, where the site coordinates are displaced by a relative amount \( \xi \), typically of the order of \( \xi_F = 0.05a \), where \( a \) is the lattice constant: this distortion asymmetrically affects the hopping matrix elements. We assume the other parameters fixed during the ferroelectric distortion, while for the \( t \) variation we assume the simple Su-Schrieffer-Heeger \([9]\) linear dependence \( t = t_0 \pm 2\alpha\xi \). For reasons given below, a realistic modeling of these materials requires a rather large electron-phonon coupling \( \alpha \), typically \( \alpha a \simeq 10 \) eV in the mean-field case. The tight-binding noninteracting Hamiltonian is trivially diagonalized as

\[
\epsilon(k) = \pm \sqrt{\Delta^2 + 4t_0^2 \cos^2 ka/2 + 16(\alpha\xi)^2 \sin^2 ka/2}.
\]  

(2)

The band structure is quadratic in \( \xi \), hence the (linear) deformation potential vanishes in the prototype structure. Nonetheless the band shift induced by the actual ferroelectric distortion \( \xi_F \) is rather large (about \(-0.8\) eV at the zone boundary) in semiquantitative agreement with LDA calculations (see \( e.g. \) Fig. 1(a) in Ref. \([3]\)).

The static charges are somewhat reduced by the distortion, as shown in Fig. 1(a), circles. When \( U \) is increased to large values, the system undergoes an interesting transition, from a band insulator to a Mott insulator. With our parameter values, the transition occurs at \( U_C = 2.27t_0 \). Egami \textit{et al.}, who first investigated this transition using only \( k = 0 \) wavefunctions, found a discontinuous drop in the static ionic charges of the prototype structure, while the charges of the ferroelectric structure were found continuous as a function of \( U \). We reproduce their results, but we also find that that the discontinuity disappears as \( k \)-point convergence is approached. A careful analysis is displayed in Fig. 1(b), which incidentally proves the effectiveness of the \( k \) average \([8]\) in getting rid of spurious finite-size effects. The apparent discontinuity is due to a level crossing which occurs at \( k = 0 \) and \textit{not} at \( k \neq 0 \), as discussed
below. We have explicitly verified that the computed discontinuity is inversely proportional to the number of \( k \) points used. Furthermore the discontinuity disappears even with a coarse mesh if the mesh is displaced on the \( k \) axis in order to avoid the \( k = 0 \) singular point: this is also shown in Fig. 1(b), open circles.

We are interested in the macroscopic polarization \( \Delta P \) induced by the distortion, when the sites are continuously displaced from the prototype structure \((\xi = 0)\) to the ferroelectric one \((\xi = \xi_F)\). We therefore need evaluating how much charge is transported along the chain during a relative displacement of the two sublattices, in a vanishing electric field \([5]\); if we choose to keep the origin fixed on a cationic site, the transport is purely electronic. The electronic charge transport is best evaluated as a geometric quantum phase, as first shown—for the explicitly correlated case—by Ortíz and Martin \([6]\). The rationale behind the geometric phase approach is that the dynamical charge is a quantum-mechanical current—hence a phase of the wavefunction—and bears in general no relationship to the modulus of the wavefunction when periodic boundary conditions are used.

The starting ingredients are again the same ground-state wavefunctions \( \Psi_0(k) \) discussed above. One then removes the Bloch-like phase upon defining \( \Phi_0(k) = \Psi_0(k) \prod \exp(-ikx_j) \), where \( x_j \) are the site coordinates. The wavefunctions \( \Phi_0(k) \) so obtained are periodic over the supercell at any \( k \), and implicitly depend on the Hamiltonian parameters. Only the dependence upon \( \xi \) and \( U \) will be relevant in the following discussion. One then defines the many-body generalization of the geometric phase first introduced by Zak \([10]\):

\[
\gamma(\xi, U) = i \int dk \langle \Phi_0(k) | \frac{\partial}{\partial k} \Phi_0(k) \rangle,
\]

where the \( k \)-integration is over the Brillouin zone of the supercell. The numerical calculation proceeds as in the uncorrelated case \([3]\), and the macroscopic polarization of the ferroelectric structure is

\[
\Delta P = [\gamma(\xi_F, U) - \gamma(0, U)]/2\pi,
\]

defined modulo a polarization quantum of magnitude 1, corresponding to the transport of
one charge over one cell. This is one half of the quantum of the mean-field theory [3], where double occupancy of one-particle states is enforced.

In the special case where the electron-phonon coupling $\alpha$ is taken as vanishing, then each site may only transport its static ionic charge (shown in Fig. 1): in fact the polarization calculated as a geometric phase accounts precisely for this rigid charge transport. Notice however that the two alternative calculations are not numerically equivalent, thus providing a useful convergence test. Using our typical $k$-point mesh given above, the error is smaller than $10^{-3}$. When $\alpha \neq 0$, the dynamical charge is no longer equal to the static one, and is typically much larger than it.

Let us first illustrate the mean-field ($U = 0$) calculation. We take $\alpha a = 10$ eV, which provides a spontaneous polarization in agreement with both measurements and LDA calculations in typical ferroelectric perovskites. The polarization $\Delta P$ is almost linear in $\xi$: the relevant quantities to display are therefore the average dynamical charge $\langle Z^*(\xi) \rangle = a\Delta P(\xi)/\xi$ and the linear (or Born) dynamical charge of the prototype structure $Z^* = aP'(0)$. The static (cationic) charge is 1.47: charge transport is enhanced by a factor larger than four by the electron-phonon coupling, thus providing giant dynamical charges, and large values of the spontaneous polarization. The actual values within our model are $\langle Z^*(\xi_F) \rangle = 5.95$ and $Z^* = 7.28$.

We now switch discussing the effects of electron-electron interaction. The first interesting phenomenon occurs already in the centrosymmetric system, having real wavefunctions $\Phi_0(k)$: the Zak phase $\gamma$ changes discontinuously by $\pi$ at the transition point. Equivalently, one finds a Berry phase of $\pi$ around the rectangular loop in the $(k, U)$ plane shown in Fig. 3, since the vertical sides of the rectangle do not contribute [5, 6]. This means that the real wavefunction undergoes a sign change when transported along the closed path: the commonest occurrence of such a feature, well known in molecular physics [11], is due to the presence of a point of double degeneracy inside the domain. This is precisely the case here: there are two well distinct states whose energies cross at the point $(0, U_C)$, whereas at $k \neq 0$ there is no degeneracy. We have numerically checked the level crossings by exploiting the metastability
of the Lanczos iteration across the transition. Coming now to the physical meaning of such transi-
tion, we notice that a phase change of $\pi$ corresponds to the transport of an electronic charge over half a lattice constant, from an oxygen site to a cationic one. Notice once more that such transport occurs without affecting the static charges. This is a virtue of the ring geometry of our chain, whereas in a finite linear chain, owing to continuity, charge transport would obviously affect the static charges of the end sites. We thus discover that the geometric phase—and not the static ionic charge—is the primary order parameter for the transition.

One could even straightforwardly generalize the “band-center operator” of Ref. [10] to the many-body case, and characterize the transition by saying that the crystalline ground state is an eigenstate of such operator belonging to different eigenvalues below and above $U_C$.

We then consider the polarization of the ferroelectric structure, calculated as in Eq. (4) and where the $\Phi_0(k)$ are complex. We plot in Fig. 2 the average dynamical charge $\langle Z^* \rangle$ as a function of $U$, for several values of $\xi$. In the moderate-$U$ region below $U_C$ the electron-electron interaction produces a significant enhancement of the polarization. Notice that this latter feature is in apparent contradiction with the fact that the static ionic charges decrease instead with increasing $U$. The most prominent feature of Fig. 2 is the divergence at $U_C$, which has an interesting physical meaning. The (near) divergent curve, corresponding to our smallest $\xi$, is an approximation to the Born dynamical charge: the figure then indicates that at $U = U_C$ an infinitesimal sublattice displacement, (starting from the prototype structure) induces a finite charge transport, hence an infinite $Z^*$. At finite $\xi$ values instead—and in particular at the value $\xi_F = 0.05a$ corresponding to a realistic ferroelectric distortion—the polarization has a finite and large discontinuity at $U_C$. Notice that the Zak phase of the ferroelectric structure is continuous as a function of $U$, and therefore both the divergence and the discontinuity of the dynamical charges must be traced back to the discontinuity of the centrosymmetric ($\xi = 0$) Zak phase in Eq. (4).

In conclusion, we have investigated here the effect of electron-electron interaction in the macroscopic polarization of ferroelectric perovskites, by means of an explicit model Hamiltonian which captures the basic features of the phenomenon, and exploiting the geo-
metric phase approach. The very large polarization of these materials owes to their mixed ionic/covalent character, and is further enhanced by electron-electron interaction, as long as its strength remains moderate. At higher strength, the system undergoes a transition from a band insulator to a Mott insulator. At the transition point, the polarization is discontinuous, and even reverses its sign for a given sublattice displacement. In the highly correlated regime the cation transports a negative dynamical charge, and oxygen a positive one.

We are grateful to E. Tosatti for many helpful discussions and for a critical reading of the manuscript. Part of this work was performed while the authors were at the Institute for Theoretical Physics, University of California at Santa Barbara. The research was supported in part by National Science Foundation under Grant No. PHY89-04035.
REFERENCES

[1] R. Resta, M. Posternak, and A. Baldereschi, Phys. Rev. Lett. 70, 1010 (1993).

[2] R.D. King-Smith and D. Vanderbilt, Phys. Rev. Lett. 72, 3618 (1994).

[3] M. Posternak, R. Resta, and A. Baldereschi, Phys. Rev. B 50, 8911 (1994).

[4] T. Egami, S. Ishihara, and M. Tachiki, Science 261, 1307 (1993); Phys. Rev. B 49, 8944 (1994); ibid. 16123 (1994).

[5] See R. Resta, Rev. Mod. Phys. 66, 899 (1994), and references quoted therein.

[6] G. Ortíz and R.M. Martin, Phys. Rev. B 49, 14202 (1994).

[7] W.A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980).

[8] C. Gros, Z. Phys. B 86, 359 (1992).

[9] W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); see also Sec. 8.5.2 in P. Fulde, Electron Correlation in Molecules and Solids (Springer, Berlin, 1991).

[10] J. Zak, Phys. Rev. Lett. 62, 2747 (1989); see also L. Michel and J. Zak, Europhys. Lett. 18, 239 (1992).

[11] C.A. Mead, Rev. Mod. Phys. 64, 51 (1992).
FIGURES

FIG. 1. Static charge of the cation as a function of the Hubbard $U$. (a) Prototype centrosymmetric structure (triangles) and ferroelectric structure (circles) below the transition. (b) Different computations for the prototype structure at the transition point $U_C$. Empty triangles: 10 $k$ points. Filled triangles: 100 $k$ points. Empty circles: 30 $k$ points, displaced such as to avoid $k = 0$.

FIG. 2. Average dynamical charge of the cation as a function of the Hubbard $U$, for different values of the displacement $\xi$. In order of increasing value of the discontinuity at $U_C$, the curves represent: $\xi = \xi_F = 0.05a$; $\xi = 0.035a$; $\xi = 0.0245a$; $\xi = 0.014a$; $\xi = 0.0035a$.

FIG. 3. Rectangular loop in the $(k, U)$ plane which encircles the level crossing at $k=0$ and $U=U_C$, in arbitrary units. The projection over the $k$ axis coincides with the Brillouin zone of the supercell. The cross is at the degeneracy point.