Many-Body Effects on Polarization and Dynamical Charges in a Partly Covalent Polar Insulator

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(Received 2 November 1994)

In a mixed ionic/covalent insulator the dynamical ionic charges are much larger than the static ones. The phenomenon is particularly relevant in ferroelectric perovskites, and is well understood at the mean-field level. Here we use a model Hamiltonian to investigate polarization in a strongly correlated, and partially ionic, insulator. Charge transport is evaluated as a Berry phase. At a critical value of the electron-electron interaction, the model has 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, the anion transports a *positive* charge.

PACS numbers: 77.80.–e, 71.10.+x, 71.27.+a

The macroscopic polarization of a dielectric material has been a major challenge to electronic-structure theorists for many years, not only on computational grounds, but even as a matter of principle. Two main advances [1] have allowed quantum-mechanical insight (at the mean-field level) into the phenomenon, and particularly into the polarization of ferroelectric perovskites [2]. In these materials a simple ionic model fails: for instance, the effective dynamical charge associated with an oxygen displacement is of the order of -6, i.e., about 3 times the nominal static value implied by a completely ionic picture [2,3] (atomic units of charge are adopted throughout). Such apparently exotic behavior is simply due to a large amount of covalence—as demonstrated at the mean-field level [4]—whereas there is no reason to suspect any major role played by correlation as far as such materials are concerned. The present Letter investigates a different facet of the problem, focusing on the polarization induced by a sublattice displacement (optical phonon) in a partially ionic material where both covalence and correlation play an important role, as is definitely the case for other interesting compounds of the perovskites family, such as, e.g., the parent compounds of the high T_c cuprates. We do not aim at modeling some particular material, while instead we show quite generally that in a correlated insulator having a mixed ionic-covalent character, electron-lattice coupling is responsible for highly nontrivial charge transport. In the strongly correlated regime, the anions transport a *positive* dynamical charge.

In order to make a correlated wave function available, we schematize the Hamiltonian of our model insulator with a one-dimensional two-band Hubbard model at half filling, first proposed by Egami, Ishihara, and Tachiki, and which—upon increase of the Hubbard U—displays a transition from a band insulator to a Mott-like insulator [5]. When we examine the transition from the standpoint of macroscopic polarization, several exotic phenomena show up. In particular, we find that the static ionic charges are continuous, whereas polarization and dynamical charges are discontinuous: therefore the Berry phase associated with macroscopic polarization [1,6] is the primary order parameter for the transition.

As usual with Hubbard-like models, the Hamiltonian may describe materials of different kinds, according to the actual choice of the parameters. Since we are going to demonstrate some novel and unexpected qualitative effects, we are not interested here in exploring a wide parameter range. The only very essential feature of the model material we are going to investigate is its mixed ionic-covalent character, on the top of which we switch electron correlation on. We take a linear chain with two atoms per cell, having in mind oxygen (O) and a generic cation (B). In order to reduce the number of parameters, when switching electron-electron interaction on, we set equal values of the Hubbard U on anion and cation. We do not expect our main qualitative findings to depend on such a (quite arbitrary) choice. The Hamiltonian of the centrosymmetric structure is therefore

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

and depends on two parameters besides U: the hopping t_0, and the difference in site energies $E_B - E_{\rm O} = 2\Delta$. 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 ± 2. The interesting parameter range is for t_0 of the order of 2Δ, which warrants a mixed ionic-covalent character. In the remainder of this study we assume $\Delta = 2$ eV and $t_0 = 3.5$ eV: this provides a $U = 0$ bandwidth of 5.3 eV, which happens to be a realistic value for the valence bands of a (three-dimensional) partly covalent polar insulator.

We plot in Fig. 1(a) the static ionic charge as a function of U (triangles). The calculations have been performed in 8-site supercells, using skew (quasiperiodic) boundary

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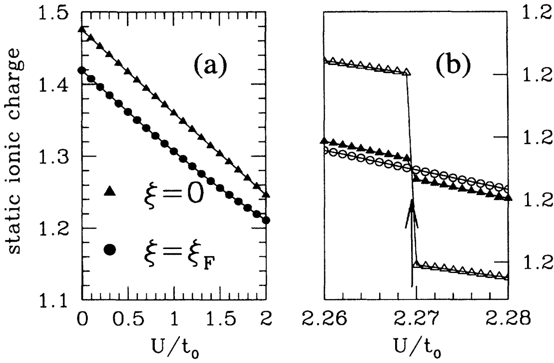

FIG. 1. Static charge of the cation as a function of the Hubbard U. (a) Centrosymmetric structure (triangles) and distorted structure (circles) below the transition. (b) Different computations for the symmetric structure at the transition point U_C. Empty triangles: 10 k points. Filled triangles: 100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

conditions on each electronic variable, and then taking the average over the boundary conditions (alias over the supercell quasimomenta k), as in Ref. [7]. 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 Lanczos algorithm, which provided the ground-state electronic wave functions $\Psi_0(k)$ 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 $4^8 = 65\,536$ elements). Use of the center-of-mass translation symmetry is also possible, but becomes useful only for larger systems. In an insulating system such as the present one the size effects are small, and further minimized by k averaging [7]. For a few parameter values we have indeed performed 12-site calculations, and checked that the results agree with the 8-site ones to within 1%, at least for the quantities studied here.

We study the dynamical charge transported along the chain by a relative displacement ξ of the two sublattices: a typical magnitude of interest (as for ferroelectrics) is $\xi_F = 0.05a$, where a is the lattice constant. Sublattice displacements asymmetrically affect the hopping matrix elements. We assume the other parameters fixed, while for the t variation we assume the simple Su-Schrieffer-Heeger [8] linear dependence $t = t_0 \pm 2\alpha\xi$. In choosing the electron-phonon coupling α we are guided again by what would be a realistic value for describing (at $U = 0$) a ferroelectric perovskite, i.e., $\alpha a = 10$ eV. We stress once more that we use a ferroelectric perovskite only as a guide to choosing a reasonable parameter set, while at $U \neq 0$ our Hamiltonian aims at modeling an unspecified insulator having mixed ionic-covalent character, *not* a ferroelectric perovskite.

The tight-binding noninteracting Hamiltonian is trivially diagonalized as

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

The band structure is quadratic in ξ, hence the (linear) deformation potential vanishes in the centrosymmetric structure. Nonetheless, the band shift induced by a displacement of magnitude ξ_F is rather large (about -0.8 eV at the zone boundary). Again, this is typical for the mean-field bands of a mixed ionic/covalent insulator [see e.g., Fig. 1(a) in Ref. [4]].

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, first discovered by Egami, Ishihara, and Tachiki, who studied an identical Hamiltonian for a somewhat different parameter range [5]. They identified the transition as a discontinuous drop in the static ionic charges of the centrosymmetric structure, while the charges of the distorted structure were found continuous as a function of U. With our parameter values, we find a qualitatively identical discontinuity at $U_C = 2.27 t_0$. However, this is not all. The discontinuity is present when only $k = 0$ wave functions are used, as in Ref. [5], while it 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 [7] in getting rid of spurious finite-size effects. The apparent discontinuity is due to a level crossing which occurs at $k = 0$ and *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 ΔP induced by a zone-center optical phonon, when the sites are continuously displaced from the centrosymmetric structure ($\xi = 0$) to a broken-symmetry one, up to $\xi = \xi_F$. We therefore need to evaluate how much charge is transported along the chain during a relative displacement of the two sublattices, in a vanishing electric field [1]; 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 wave function—and bears in general *no relationship* to the modulus of the wave function when periodic boundary conditions are used [1].

The starting ingredients are again the same ground-state wave functions $\Psi_0(k)$ 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 wave functions $\Phi_0(k)$ so obtained are *periodic* over the supercell at any k, and implicitly depend on the Hamiltonian parameters. Only the dependence upon ξ and U will be relevant in the following discusssion. One then defines the many-body generalization of the geometric phase first introduced by Zak [9]:

$$\gamma(\xi, U) = i \int dk \left\langle \Phi_0(k) \left| \frac{\partial}{\partial k} \Phi_0(k) \right. \right\rangle, \qquad (3)$$

where the k integration is over the Brillouin zone of the supercell. The numerical calculation proceeds as in the uncorrelated case [1], and the macroscopic polarization of the distorted structure is

$$\Delta P = [\gamma(\xi_F, U) - \gamma(0, U)]/2\pi, \qquad (4)$$

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 [1], where double occupancy of one-particle states is enforced.

In the special case where the electron-phonon coupling α 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 30 k points, the error is smaller than 10^{-3}. When $\alpha \neq 0$, the dynamical charge is no longer equal to the static one, and typically much larger than it in partly covalent polar crystals.

Let us first illustrate the noninteracting calculation. The polarization ΔP is almost linear in ξ: 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 centrosymmetric structure $Z^* = aP'(0)$. The static (cationic) charge is 1.47: charge transport is enhanced by a factor larger than 4 by the electron-phonon coupling, thus providing giant dynamical charges and large polarization values. The actual values within our model are $\langle Z^*(\xi_F)\rangle = 5.95$ and $Z^* = 7.28$.

We then switch electron-electron interaction on. The first interesting phenomenon occurs already in the centrosymmetric model system, where the Zak phase γ changes discontinuously by π at the transition point. Equivalently, one finds a Berry phase of π around the rectangular loop in the (k, U) plane shown in Fig. 2, since the vertical sides of the rectangle do not contribute [1,6]. This means that the wave function undergoes a sign change when transported along the closed path: the commonest occurrence of such a feature, well known in molecular physics [10], 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 $k \neq 0$ the ground state is nondegenerate. We have numerically checked the level crossings by exploiting the metastability of the Lanczos iteration across the transition; we have also verified that the ground state is a spin singlet both below and above the transition. Coming now to the physical meaning of such transition, we notice that a phase change of π 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. [9] to the many-body case, and characterize the transition by saying that the crystalline ground state is an eigenstate of such an operator belonging to different eigenvalues below and above U_C.

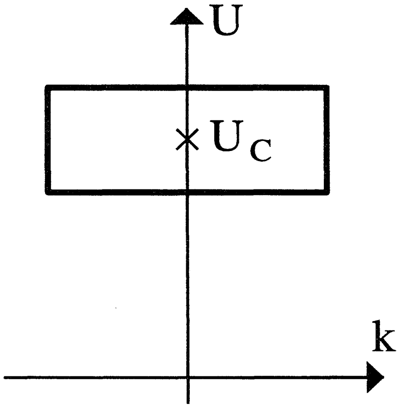

FIG. 2. Rectangular loop in the (k, U) plane which encircles the level crossing at $k = 0$ and $U = U_C$, in arbitrary units. The projection over the k axis coincides with the Brillouin zone of the supercell. The cross is at the degeneracy point.

We then consider the polarization of the distorted structure, calculated as in Eq. (4). We plot in Fig. 3 the average dynamical charge $\langle Z^*\rangle$ as a function of U, for several values of ξ. In the moderate-U region below U_C the electron-electron interaction enhances 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. 3 is the divergence at U_C, which has an interesting physical meaning. The (near) divergent curve, corresponding to our smallest ξ, is an approximation to the Born dynamical

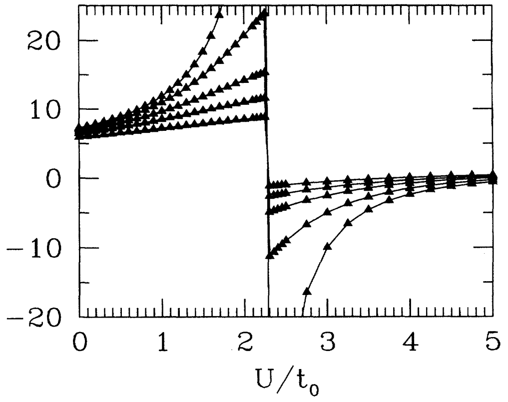

FIG. 3. Average dynamical charge of the cation as a function of the Hubbard U, for different values of the displacement ξ. In order of increasing value of the discontinuity at U_C, the curves represent $\xi = \xi_F = 0.05a$, $\xi = 0.035a$, $\xi = 0.0245a$, $\xi = 0.014a$, and $\xi = 0.0035a$.

charge: the figure then indicates that at $U = U_C$ an infinitesimal sublattice displacement (starting from the symmetric structure) induces a *finite* charge transport, hence an infinite Z^*. At finite ξ values instead the polarization, Eq. (4), has a finite and large discontinuity at U_C. Notice that the Zak phase of the distorted 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 a mixed ionic/covalent insulator, by means of an explicit model Hamiltonian, and exploiting the geometric phase approach. The very large polarization and dynamical charges of such an insulator are 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-like insulator. At the transition point, charge transport 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 the anion 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 the National Science Foundation under Grant No. PHY89-04035.

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