

Termination effects in electric field polarization of periodic quasi-one-dimensional systems

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For a long finite chain with repeated units it is demonstrated that terminal substitution can change the dipole moment per unit. On the other hand, the dipole moment per unit is known to be essentially a bulk property accessible through crystal orbital calculations on the corresponding infinite periodic system which, by construction, does not have terminal regions. This seeming contradiction is resolved by relating the accumulated charge at the ends of a finite chain to an apparently arbitrary, and nonphysical, integer associated with the phase of the crystal orbitals. Model one-dimensional calculations show that the measurable structural responses of a finite chain to an electrostatic field can be exactly reproduced by an infinite periodic treatment of the same system. The field is seen to affect the lattice constant and, thereby, the internal structural parameters.

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I. INTRODUCTION

A detailed understanding of the response of materials to electromagnetic fields is essential to their spectroscopic characterization and application in linear and nonlinear optics. For processes involving low-frequency fields, either alone or in combination with optical fields, both the structural (i.e., nuclear) and electronic responses are important. In this regard the total dipole moment, including both permanent and induced contributions, is the key carrier of information. Although it is straightforward to calculate this property for any finite system, it is only in the last couple of decades that appropriate computational procedures for systems that can be considered as infinite and periodic have been presented.

In the present work we shall concentrate on a large (macroscopic) quasi-one-dimensional (1D) material that consists of a sequence of identical building blocks (units) which deviate from regularity only in the terminating regions. Since the number of units in the terminations relative to the total is very small, it is a good approximation for most purposes to neglect the terminations and treat the material as an infinite, periodic system. In the thermodynamic limit the (intensive) property per unit corresponding to the extensive property $\xi(N)$, may be determined as (N is the total number of units)

$$\bar{\xi} = \lim_{N \rightarrow \infty} \frac{\xi(N)}{N} = \lim_{N \rightarrow \infty} \frac{1}{\Delta N} [\xi(N + \Delta N) - \xi(N)]. \quad (1)$$

For our discussion we will be particularly interested in the total energy per unit as well as the dipole moment per unit. The latter is related to the polarization,

$$\vec{P} = \frac{1}{a} \vec{\mu}, \quad (2)$$

where a is the length of one unit. In the case of two- or three-dimensional (2D or 3D) materials the length is replaced by the area or volume as appropriate.

The question of whether terminations or surfaces influence the polarization has been the subject of discussion for several decades.¹⁻⁸ A rigorous formulation establishing that polarization is a bulk property was, finally, presented by Vanderbilt and King-Smith.⁸ Nonetheless, there remains a

sense in which it is surface dependent. Thus, as we will demonstrate here, the termination of 1D chains can influence experimental observables determined by the polarization. Specifically, we show that the lattice constant in the inner part of an extended 1D system exposed to a uniform longitudinal electrostatic field may be altered by changing the terminations. The same is true of internal structural parameters as well. Most importantly, we also present a procedure for determining this effect from calculations on the corresponding infinite periodic system.

As pointed out, for example, by Souza *et al.*,⁹ one may distinguish between the response of the structure with respect to either the macroscopic field strength or the potential drop across each lattice vector. As our treatment shows, in 1D the former is surface dependent whereas the latter is not.

An experimental realization of the surface-dependent case may be obtained by considering a long chain like that of Fig. 1, placed between two electrodes. Applying a potential between the two electrodes, the length of the chain will change. This change is monitored during the experiment and may, in general, be partly due to changes in the length of the bulk region and partly due to changes in the lengths of the units in the terminations. Often the change in length due to the terminations can be neglected in comparison with the macroscopic effect arising from the change in the bulk lattice constant, a . Sometimes, however, we have found that such will not be the case. In either event the contribution from the terminations can be accounted for by determining the chain length dependence of the structural response. Then, a plot of the change in length per bulk unit versus the fixed field strength, \mathcal{E}_{dc} , can be used to obtain the zero-field limit $\left. \frac{da}{d\mathcal{E}_{dc}} \right|_{\mathcal{E}_{dc}=0}$. We shall demonstrate that this change, which can

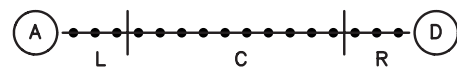


FIG. 1. Schematic representation of a long but finite, regular chain. Each filled circle, placed regularly along the chain axis (the z axis), represents a building block containing one or more atoms. Donor and acceptor groups (D and A) may be included at the terminations. The separation into a central (C) and two terminal (L and R) regions is indicated by the vertical lines.

be experimentally obtained,¹⁰ depends on the terminations.

Alternatively, one may also study the change in the lattice constant for fixed potential drop over one unit cell. This response does not depend on the terminations. Thus, the two measurements, which are both feasible, contain complementary information. From a theoretical point of view, both responses can also be calculated.

II. THEORY

During the last two decades a mathematically rigorous way to treat polarization has been developed through the Berry phase approach [modern theory of polarization (MTP)] (Refs. 8 and 11–14) and the related (see Refs. 14 and 15) vector potential approach (VPA),^{16,17} with the latter based upon earlier work by Blount¹⁸ and by Genkin and Mednis.¹⁹ As background we begin by briefly reviewing some key results from these treatments and, then, turn to our analysis and illustrative calculations for the case of a system extended in 1D.

A schematic representation of a long but finite 1D chain is shown in Fig. 1. It is useful to split this system into three distinct spatial parts, a perfectly regular central region (C) where the electrons do not feel the finite size of the system, and two terminal regions (L and R). The component of the dipole moment per unit along the (z) chain axis can be defined as

$$\bar{\mu} = \lim_{N \rightarrow \infty} [\mu(N+1) - \mu(N)], \quad (3)$$

where N is the number of units in the chain and μ is the z component of the total dipole moment. With the spatial separation above we have^{20,21}

$$\begin{aligned} \mu = & \int_L \rho(\vec{r})z d\vec{r} + \int_C \rho(\vec{r})z d\vec{r} + \int_R \rho(\vec{r})z d\vec{r} = N_C \mu_C \\ & + \left[z_R \int_R \rho(\vec{r}) d\vec{r} + z_L \int_L \rho(\vec{r}) d\vec{r} \right] \\ & + \left[\int_L \rho(\vec{r})(z - z_L) d\vec{r} + \int_R \rho(\vec{r})(z - z_R) d\vec{r} \right] \end{aligned} \quad (4)$$

in which $\rho(\vec{r})$ is the total charge density, μ_C is the z component of the dipole moment of a (neutral) central unit and N_C is the number of units in C . Finally, z_R and z_L describe the centers of nuclear charge in the R and L regions, respectively. Assuming that the entire system is neutral, a combination of Eqs. (3) and (4) gives (see Ref. 20)

$$\bar{\mu} = \mu_C + Q_R \cdot a, \quad (5)$$

where $Q_R (= -Q_L)$ is the total charge in R (L), and a is the unit-cell lattice constant of C . According to this expression the dipole moment per unit depends on the charge accumulated in the terminal regions which, at first glance, can vary widely.

There are, however, restrictions on the surface charges as Vanderbilt and King-Smith⁸ have shown. They write the electronic part of the dipole moment in terms of localized orbitals w_{lp}

$$\mu_e = \sum_l \sum_p \int |w_{lp}(\vec{r})|^2 z d\vec{r}, \quad (6)$$

where w_{lp} , the p th orbital localized to the l th unit, is obtained by a unitary transformation of the occupied canonical orbitals. Then, using the idempotency of the density matrix, it is proved that the number of electrons associated with the terminal regions must be integral. On this basis, the dipole moment per unit (and, consequently, the polarization) is essentially a bulk property with quantized values that differ from one another only by lattice vectors.^{20,22} It follows that this property is accessible (modulo a lattice vector) through a conventional band-structure calculation on an infinite periodic system, even though there are no terminations (per construction) in the latter case.

For a 1D periodic system the electronic orbitals may be written as

$$\psi_j(k, \vec{r}) = e^{ikz} u_j(k, \vec{r}), \quad (7)$$

where j is a band index and $u_j(k, \vec{r})$ is lattice periodic. Usually, a finite set of K equidistant k points in the interval $[-\frac{\pi}{a}; \frac{\pi}{a}]$ is employed in a band-structure calculation. According to both the MTP and VPA treatments one may write the electronic part of the static dipole moment per unit as^{12,15,23}

$$\bar{\mu}_{\text{KSV}} = \frac{i}{K} \sum_{k=1}^K \sum_{j=1}^B \langle u_j(k) | \frac{\partial}{\partial k} u_j(k) \rangle. \quad (8)$$

In Eq. (8) B is the number of singly occupied bands (we assume that there is a gap between occupied and empty orbitals and allow for spin-up and spin-down orbitals to be different). The total dipole moment per unit is obtained by adding the contribution from the nuclei in the zeroth unit cell.

In Eq. (7) the orbitals may be modified by band and k -dependent phase factors,

$$\psi_j(k, \vec{r}) \rightarrow e^{i\phi_j(k)} \psi_j(k, \vec{r}) \quad (9)$$

in which

$$\phi_j(+\pi/a) - \phi_j(-\pi/a) = n_j \cdot 2\pi \quad (10)$$

since

$$e^{i\phi_j(+\pi/a)} = e^{i\phi_j(-\pi/a)}. \quad (11)$$

Thus, $\bar{\mu}$ contains an unknown, additive constant, $n \cdot a$, with $n = \sum_j n_j$.

For both the extended but finite, system and the infinite periodic model for this system the dipole moment per unit may be changed by an integer multiple of the unit cell lattice constant. However, the origin of the integer is quite different in the two cases. For the finite chain it has a physical origin determined by the terminations which govern the charge accumulated at the chain ends. Accordingly, the integer is fixed by the electronic structure. For the infinite periodic model the integer is related to a mathematical ambiguity in the phase of a complex number and is completely arbitrary. Here we demonstrate that a fixed choice of the integer for the infinite periodic system corresponds to modeling a finite chain with a specific charge in the terminal region. We do

this by considering a long finite oligomeric chain with different terminations (see Fig. 1) and, as a result, different charge accumulation at the chain ends. When exposed to electrostatic (dc) fields different electronic and structural response properties are obtained. It is, then, shown that all such properties can be reproduced by maintaining an appropriate fixed value of n in corresponding model infinite periodic chain calculations.

III. COMPUTATIONAL APPROACH

In order to perform extensive calculations, and to avoid truncation and other numerical errors, we use a model Hamiltonian similar to the ones employed in earlier studies.^{15,21,24} In doing so we emphasize that no attempt is made to reproduce results for any real system but that the model Hamiltonian contains all important features of a parameter-free electronic-structure calculation.

Our system is a linear chain with an $-A=B$ -repeat unit that has alternating atoms and bond lengths. There are four electrons per repeat unit and the nuclear charges are each $+2$. For the infinite periodic chain two parameters describe the structure. One is the lattice parameter a and the other is a parameter u that describes the bond-length alternation, i.e., the two atoms of the n th unit cell are placed at

$$z = \mp \frac{a}{4} + n \cdot a \pm u, \quad (12)$$

where the upper (lower) sign is used for the A (B) atoms. Predetermined values for the field-free structural constants u and a are obtained by adding an elastic contribution to the electronic energy. This contribution contains terms of second and fourth order in the nearest and next-nearest bond lengths,

$$E_{\text{elastic}} = \frac{f_1}{2} \sum_i \left(z_i - z_{i-1} - \frac{d_0}{2} \right)^2 + \frac{f_3}{4} \sum_i \left(z_i - z_{i-1} - \frac{d_0}{2} \right)^4 + \frac{f_2}{2} \sum_i (z_i - z_{i-2} - d_0)^2 + \frac{f_4}{2} \sum_i (z_i - z_{i-2} - d_0)^4. \quad (13)$$

Here z_i is the z coordinate of the A atom of the $\frac{i+1}{2}$ th unit cell for odd i and of the B atom of the $\frac{i}{2}$ th unit cell for even i . The parameters of this function (i.e., f_1, f_2, f_3, f_4 , and d_0) are varied so that the field-free optimized geometry gives the desired values for a and u . In the finite chain calculations the structure of the central part of the chain containing N units is used for comparison with the infinite periodic chain as follows [the notation is the same as in Eq. (13)],

$$a = \frac{1}{2} [(z_{N+1} - z_{N-1}) + (z_{N+2} - z_N)]$$

$$u = \frac{\pm 1}{8} [z_{N+2} - 3z_{N+1} + 3z_N - z_{N-1}] \quad (14)$$

with the upper (lower) sign in the second identity for odd (even) N . When the finite chain is sufficiently long the values of a and u so obtained agree with those of the infinite periodic chain. The origin of the coordinate system is chosen as

the arithmetic average of all nuclear positions for the finite chains and as that of all nuclei in the Born von Kármán zone for the infinite, periodic chains.

For the calculation of electronic properties a restricted Hartree-Fock-type approximation is used as well as a basis set of orthonormal atom-centered functions with two functions per atom denoted by ζ_{lXp} where p is the basis function on atom X of the l th unit, i.e., $p=1, 2$ and $X=A$ or B . Corresponding to each spatial orbital ζ_{lXp} there are two spin-orbitals $\zeta_{lXp}\alpha$ and $\zeta_{lXp}\beta$.

We let \hat{h}_0 be the field-free one-electron operator and \hat{v} the two-electron operator. The one-center one-electron term $\langle \zeta_{lXi} \sigma | \hat{h}_0 | \zeta_{lXj} \sigma \rangle$ is taken to be nonzero only if $i=j$. Moreover, the two-center matrix elements are assumed to vanish except for those between functions that have the same spin and are located on neighboring atoms. These nonvanishing elements are taken to vary linearly as a function of interatomic distance. For each of the four pairs of nearest-neighbor basis functions there are, accordingly, two parameters. Finally, for simplicity, the only two-electron terms retained are $\langle \zeta_{lXi} \sigma_1 \zeta_{lXi} \sigma_2 | v | \zeta_{lXi} \sigma_1 \zeta_{lXi} \sigma_2 \rangle$.

For the finite chain the dc field is included in the electronic Hamiltonian through the term $-\sum_i \mathcal{E}_{\text{dc}} z_i$, where z_i is the z coordinate of the i th electron, \mathcal{E}_{dc} is the amplitude of the dc field, and we have set the magnitude of the elementary charge $|e|=1$. It turns out to be important for this term that the matrix elements of the dipole moment operator are consistent with the overlap matrix elements. This is most conveniently achieved by fixing the spatial form of the basis functions which, for simplicity are chosen to be: $\zeta_{lX1}(z) = \frac{1}{\sqrt{w_{X1}}}$ for $|z - z_0| \leq \frac{w_{X1}}{2}$, and zero elsewhere; $\zeta_{lX2}(z) = \frac{1}{\sqrt{w_{X2}}}$ for $-\frac{w_{X2}}{4} \leq |z - z_0| \leq \frac{w_{X2}}{2}$, and zero elsewhere, where z_0 is the position of the atom X in the l th unit. The widths, w ($w_{X1} > w_{X2}$), are kept sufficiently small so that functions on non-neighboring atoms do not overlap.

For the infinite periodic chains the dc field is included by means of the VPA methodology.^{16,17} This treatment, presented originally within a perturbation theory framework,²⁵ has been developed over the past few years into an efficient working machinery for automatically calculating the response of structural and electronic degrees of freedom to a finite static field.^{15,21,24} If the crystal orbitals are written in the form

$$\psi_j(k, \vec{r}) = \sum_{X,p} C_{X,p,j}(k) \frac{1}{\sqrt{K}} \sum_l e^{ikal} \zeta_{lXp}(\vec{r}) \quad (15)$$

then the orbital coefficients are obtained by solving the equations^{15-17,21,24}

$$\left\{ \underline{F}(k) - \mathcal{E}_{\text{dc}} \cdot \left[\underline{M}(k) + i \underline{S}(k) \frac{d}{dk} \right] \right\} \cdot \underline{C}_j(k) = \epsilon_j(k) \cdot \underline{S}(k) \cdot \underline{C}_j(k), \quad (16)$$

where $S_{qp}(k)$, $M_{qp}(k)$, and $F_{qp}(k)$ are the overlap, unit cell dipole, and Fock (or Kohn-Sham) matrix elements, respectively. In other words, the finite chain dipole moment matrix is replaced by the quantity in square brackets in Eq. (16). This introduces a $\frac{d}{dk}$ term and, thus, Eq. (16) does not corre-

spond to a normal matrix-eigenvalue problem. In order to obtain a solution we have developed an efficient and numerically stable protocol^{15,21,24} which will not be discussed here except for one aspect. Our treatment is based on a smoothing procedure whereby $C_j(k)$ is modified by a band (j) and k -dependent phase factor, making the evaluation of $\frac{d}{dk}C_j(k)$ numerically stable. With this approach the phases of $C_j(k)$ are continuous as a function of k . This makes it possible to use analytical expressions for the derivatives of the total energy as a function of structure even when $\mathcal{E}_{dc} \neq 0$.¹⁵

The dipole moment per unit of the infinite periodic system, which is determined by the operator in square brackets in Eq. (16), will lie in a certain range of length a . In order to modify this range by an integer times a , the orbitals of one or more bands are given additional phase factors, e^{iakn_j} , with n_j being an integer. Then, the phases become discontinuous across the boundary of the Brillouin zone, although the phase factors remain continuous. This leads to an additional term, $-\mathcal{E}_{dc}\sum_j n_j = -\mathcal{E}_{dc}n$, in the derivative of the total energy with respect to the lattice parameter a .

For the finite chain Eq. (1) is used to determine the dipole moment per unit. We found that chains of length $N=40$ and $N=41$ were sufficient to achieve convergence. For the infinite periodic chains $K=80$ k points were used. Finally, in order to obtain different terminations for the finite chains we modified the on-site energies $\langle \zeta_{1Ai} | \hat{h}_0 | \zeta_{1Ai} \rangle$ and $\langle \zeta_{NBi} | \hat{h}_0 | \zeta_{NBi} \rangle$ for $i=1,2$. In the calculations below this allowed us to change the charge at the chain ends by ± 2 electrons.

IV. RESULTS

We now present our findings. In Fig. 2 the different symbols in each panel correspond to periodic chain calculations for different values of the integer n . The full lines are finite chain values for charge accumulation of either 0 or +2 electrons as compared to the case where the charge in the chain terminations is similar to that of the central region.

The bottom panel shows the field-dependent dipole moment per unit at the optimized geometry. In the periodic chain calculations the integer was chosen so that the dipole moment coincides with the finite chain value at zero field. For different n (or different charge) there is a large difference in the dipole moment. In order to fit all our results in one panel we have shifted the calculated values by a constant, namely, an integer multiple of a_0 . Evidently, the periodic and representative finite chain results coincide (within numerical accuracy) at all fields. The panel just above the bottom one gives the number of electrons (i.e., the Mulliken gross populations) on one of the central A atoms obtained for the same set of calculations. Again, the infinite periodic chain results and the finite chain values are identical at all fields.

The two upper panels display the optimized structural parameters for the periodic chains. Both parameters show a clear dependence on the value of n , i.e., on the range inside which the dipole moment per unit is required to lie. This is consistent with the other panels and with the differing chemical nature of the finite chain that is being simulated. The corresponding finite chain results (solid lines; for dotted lines

see below) obtained from Eq. (14) once more agree with the periodic chain values.

The fact that the structure depends on n can easily be seen by expanding the total energy per unit, \bar{E} , about the field-free value through second order in terms of the lattice constant (a), internal structural parameter (u), and \mathcal{E}_{dc} ,

$$\begin{aligned} \bar{E} \equiv \bar{E}_{\mathcal{E}}(a, u, \mathcal{E}_{dc}) &\simeq \bar{E}_{\mathcal{E},0} + \mathcal{E}_{dc} \frac{\partial \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc}} + \frac{1}{2}(a - a_0)^2 \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial a^2} \\ &+ \frac{1}{2}(u - u_0)^2 \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u^2} + (u - u_0)(a - a_0) \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u \partial a} \\ &+ \frac{1}{2} \mathcal{E}_{dc}^2 \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc}^2} + \mathcal{E}_{dc}(a - a_0) \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial a} + \mathcal{E}_{dc}(u - u_0) \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial u}. \end{aligned} \quad (17)$$

We have added a subscript \mathcal{E} here to emphasize that the field, rather than the voltage (see later), is considered as the independent variable. This corresponds to an experimental setup where different materials that may possess different macroscopic changes in size due to the electrostatic field are experiencing the same field strength.

With the expansion of Eq. (17) one may derive an approximate expression for the change in the lattice parameter due to a given electrostatic field by setting the derivative $\frac{\partial \bar{E}_{\mathcal{E}}}{\partial a} = 0$ at the field value and the same may be done for the internal structural parameter. The result of solving this pair of coupled simultaneous equations can be expressed in terms of the piezoelectriclike coefficients $d_{a,\mathcal{E}} = \left. \frac{da}{d\mathcal{E}_{dc}} \right|_{\mathcal{E}_{dc}=0}$ and $d_{u,\mathcal{E}} = \left. \frac{du}{d\mathcal{E}_{dc}} \right|_{\mathcal{E}_{dc}=0}$

$$\begin{aligned} d_{a,\mathcal{E}} &= \left[\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial u} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u \partial a} - \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial a} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u^2} \right] \\ &\times \left[\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial a^2} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u^2} - \left(\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u \partial a} \right)^2 \right]^{-1} \\ d_{u,\mathcal{E}} &= \left[\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial a} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u \partial a} - \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial a^2} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial u} \right] \\ &\times \left[\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial a^2} \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u^2} - \left(\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial u \partial a} \right)^2 \right]^{-1}. \end{aligned}$$

Since the dipole moment per unit, $\bar{\mu} = -\frac{\partial \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc}}$ contains a contribution equal to na the partial derivative $\frac{\partial \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{dc} \partial a}$ depends upon n . Hence, both piezoelectriclike coefficients will depend upon this integer.

The coefficients obtained from Eq. (18) were used to calculate the first-order (in the field) structural changes. From the results shown in Fig. 2 it is seen (cf. dotted lines) that these simple estimates agree well with the ‘‘exact’’ results.

The dependence of the bulk quantities on the surfaces is solely due to the fact that the lattice parameter depends on n . This can be seen by repeating the periodic chain calculations of Fig. 2 but with this parameter fixed at the field-free value,

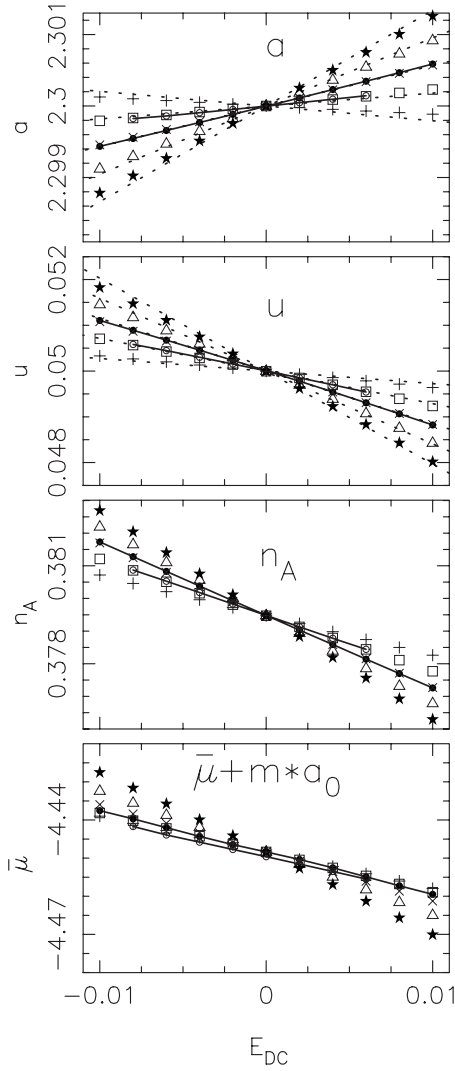


FIG. 2. Results from the model Hamiltonian calculations for finite chains with $N=40$ units and for periodic chains with 80 k points. For the periodic chains the different symbols represent results for different values of the integer n whereas the full lines show representative (see text) finite-chain results. From the top to the bottom the panels show the optimized lattice constant a , the internal structural parameter u , the number of electrons on the central A atom relative to the neutral case and the adjusted dipole moment per unit. In the two upper panels the dotted lines represent estimates from Eq. (18). In the lowest panel we have added an integer (m) times the field-free lattice constant in order to facilitate a comparison between the different results.

a_0 . The results in Fig. 3 show that all symbols fall on the same curve. Thus, all values of n lead to the same results. Moreover, by comparing with Fig. 2 it is seen that relaxing a leads, in general, to considerably stronger property variations, as a function of field strength, than just relaxing u .

So far we have considered how the structural parameters change as a function of the field strength. In particular, the analog of $da/d\mathcal{E}_{dc}$ for thin films can be determined by phase modulation measurements.¹⁰ Alternatively, one may determine the variation in the structural parameters as a function of the voltage. Assuming that the length of the macroscopic

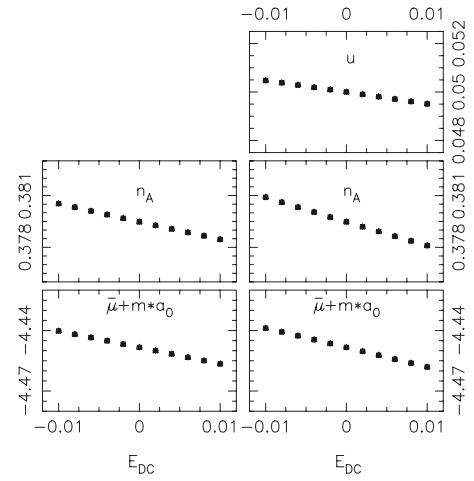


FIG. 3. Results from model Hamiltonian calculations with fixed lattice parameter. The left panels are for the initial structure and the right ones after relaxing u .

chain in the absence of the field equals L ($L \gg a_0$), the total potential across the sample, V_{ext} is given by

$$V_{\text{ext}} = \frac{L}{a_0} V_{\text{dc}} = \frac{La}{a_0} \mathcal{E}_{\text{dc}}. \quad (19)$$

Here V_{dc} is the potential drop over one unit cell, i.e., $a \cdot \mathcal{E}_{\text{dc}}$. In an experiment where different samples are exposed to the same external voltage, V_{ext} or V_{dc} , the field strength will generally be different. For that case, we express \bar{E} in terms of the independent variables V_{dc} , a , and u . This leads to the piezoelectriclike coefficients defined as $d_{a,v} = a_0 \frac{da}{dV_{\text{dc}}} \big|_{V_{\text{dc}}=0}$ and $d_{u,v} = a_0 \frac{du}{dV_{\text{dc}}} \big|_{V_{\text{dc}}=0}$. These coefficients have the same dimension as those of Eq. (18). After transforming the analog of Eq. (17) to the same set of partial derivatives that appear in the latter, it turns out that $d_{a,v}$ and $d_{u,v}$ are given by the same expressions as in Eq. (18) except for the replacement

$$\frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{\text{dc}} \partial a} \rightarrow \frac{\partial^2 \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{\text{dc}} \partial a} - \frac{1}{a_0} \frac{\partial \bar{E}_{\mathcal{E}}}{\partial \mathcal{E}_{\text{dc}}} = - \left(\frac{\partial \bar{\mu}}{\partial a} - \frac{\bar{\mu}}{a} \right) \bigg|_{a=a_0}. \quad (20)$$

This term is independent of n and, consequently, the dependence of the responses ($d_{a,v} = a_0 \frac{da}{dV_{\text{dc}}} \big|_{V_{\text{dc}}=0}$ and $d_{u,v} = a_0 \frac{du}{dV_{\text{dc}}} \big|_{V_{\text{dc}}=0}$) on the surfaces is removed.

V. CONCLUSIONS

In short, the purpose of the present paper was twofold. (1) We have demonstrated that, for a long finite chain with repeated units, the structural responses to an external applied field of fixed strength depends upon the charge at the chain ends which, in turn, is governed by the terminations. Different terminations of an otherwise identical chain can lead to different responses. In passing we note that different responses will be observed only if the field is held constant rather than the potential drop over a unit cell. (2) Although an infinite periodic chain does not have terminations, the

effect of introducing such terminations is indirectly included in the MTP/VPA crystal orbital treatment through an (undefined) integer, n , that appears in the boundary conditions for the crystal orbitals. Thus, this arbitrary integer has now been linked to a physical observable.

The dependence of the structural responses to an electrostatic field described above arises because the general expression for the electronic dipole moment per unit contains a term given by the integer, n , multiplied by the lattice constant and the latter couples mechanically with the internal structural parameters of the unit cell. If the lattice parameter is fixed, then the internal structural responses are suppressed. By chemically modifying the terminations (for example, by attaching specifically designed ligands) one can modify the integer and thereby observe an effect on the piezoelectric properties.

Theoretical arguments show that the dipole moment per unit cannot be changed arbitrarily but only by an integer multiple of a lattice vector (times the elementary charge). This is borne out here by calculations on a model system, i.e., long but finite, chains. In simulating the same system through an infinite periodic treatment we have shown that all physical effects can be reproduced “exactly” by making a specific choice for an integer related to a mathematical phase ambiguity that occurs in determining the crystal orbitals. Thus, an integer quantity, previously considered to be unphysical, has been related to an observable physical surface effect.

One may understand this result as follows. For the infinite, periodic system, the expression Eq. (8) is equivalent to

$$\bar{\mu}_{\text{KSV}} = \sum_P \int |w_{lp}(\vec{r})|^2 z d\vec{r}, \quad (21)$$

i.e., an expression very similar to that of Eq. (6). In Eq. (21) l refers to a given unit cell to which the Wannier function w is localized. Since the units per construction have to be neutral we may choose any value of l . A substitution like that of Eqs. (9) and (10) leads to a displacement of the Wannier function by n_j lattice constants, implying that $\bar{\mu}_{\text{KSV}}$ changes by $n_j a$.

For the large but finite system we may use Eqs. (4)–(6). In the central region, the w functions can be chosen as being identical to the Wannier functions that we have for the infinite, periodic system. Thus, changing the phases as in Eqs.

(9) and (10) will shift all Wannier functions in the central region by one or more lattice constants. This means that one of the boundary regions between the central region and the terminations will have less electrons whereas the other will have more electrons. Since the dipole moment per central unit is unaltered the displaced Wannier functions lead to a total dipole moment per unit that, according to Eq. (5), is identical to that of another large but finite chain with other charges at the terminations.

It has been shown elsewhere¹⁷ that (hyper) polarizabilities of infinite periodic systems do not depend upon surface charge if the structure is fixed. They will do so, however, due to structural changes induced by an electrostatic field. Moreover, the effects of the latter on experimental properties can be quite large (see, for example, Ref. 26 and references cited therein). Finally, even the charge distribution in the central region (also experimentally accessible and here quantified through the net number of electrons on atom A) depends on n for $\mathcal{E}_{\text{dc}} \neq 0$. Our numerical model studies have shown that piezoelectric surface effects can be quite significant.

In this paper we have focused on the response of the system to a given dc field, which was found to depend on the surfaces. This is not the case for a given potential drop. A physical explanation for the difference between the two quantities is as follows. In both instances the dipole moment depends upon the surface charge [cf. Eq. (5)] as does the nuclear response to an electrostatic field. However, by fixing the potential drop over a unit cell, the effects of the strain that might be induced by the surface charge and that will be different for different surface charges are eliminated. On the other hand, if the field strength is fixed, these effects have to be taken into account.

In this work we have confined ourselves to 1D systems. Naturally, the same issues arise in the case of 2D films and 3D solids. In future work we plan to consider how our 1D results may be extended to the latter.

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