Electronic Polarization in Quasilinear Chains

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Abstract

Starting with a finite \( k \)-mesh version of a well-known equation by Blount, we show how various definitions proposed for the polarization of long chains are related. Expressions used for infinite periodic chains in the ‘modern theory of polarization’ are thereby obtained along with a new single particle formulation. Separate intracellular and intercellular contributions to the polarization are identified and, in application to infinite chains, the traditional sawtooth definition is found to be missing the latter. For a finite open chain the dipole moment depends upon how the chain is terminated, but the intracellular and intercellular polarization do not. All of these results are illustrated through calculations with a simple Hückel-like model.

Key words: Polarization, Chains, Dipole moment, Single-particle model

The purpose of this Letter is to answer some questions that arise in connection with the theoretical treatment of macroscopic polarization in quasi-one dimensional chains. In order to specify the issues let us consider a macroscopic, open-ended, polymeric chain consisting of identical unit cells. For sake of argument this chain is assumed to be polarized due to an asymmetric unit cell and/or an external electric field. There are two contributions to the polarization \( P \), i.e. to the dipole moment per unit cell. One is due to the asymmetric charge distribution within a unit cell in the central region of the chain and the other is due to the charge of opposite sign that accumulates at the chain ends. Hückel-type calculations (see below) show that the contribution due to the finite chain ends does not vanish even in the infinite chain limit. This is simply due to the fact that, for a charge of fixed magnitude at either end, the dipole moment is directly proportional to the distance between the charges.

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Next, imagine that the chain ends are connected to form a ring. In that event there are no ends and all the unit cells are identical. What is the relationship between the unit cell charge distribution of the closed chain and the unit cell charge distribution at the center of the open chain? In fact, they are the same as our Hückel-type calculations confirm. Then, what has happened to the contribution to the polarization associated with the charge build-up at the ends of the open chain? As it turns out this contribution is associated with a charge flow term that arises from Blount’s theoretical expression [1] for the polarization when periodic boundary conditions are applied. This raises the question of whether or not such a term can be accounted for by the conventional sawtooth approach [2,3]. The latter is based on using a finite mesh in \( k \)-space, along with periodic boundary conditions [4,5], but it does not correspond to a finite-mesh analogue of Blount’s formula which will be presented here. From a general formulation of this analogue several approximations will be developed including the fundamental equation(s) of the so-called modern theory of polarization [6,7,8,9,10].

Using a Hückel model, discussed below, we demonstrate quantitatively that the sawtooth approach omits the current term and that Blount’s formula gives an accurate approximation for the polarization when applied with a finite set of \( k \) points. Finally, it will be seen that the polarization of long finite chains with arbitrary terminal substituents does not depend on the nature of these substituents even though the same cannot be said of the dipole moment \( D \) itself.

For a finite chain of alternating A and B atoms the Hückel Hamiltonian may be written in terms of orthonormal atom-centered basis functions \( \{\chi_p\} \) as

\[
\hat{H} = \sum_{p=-2K+1}^{2K} \epsilon_p \hat{c}_p^{\dagger} \hat{c}_p - \sum_{p=-2K}^{2K-1} t_{p,p+1}(\hat{c}_{p+1}^{\dagger} \hat{c}_p + \hat{c}_p^{\dagger} \hat{c}_{p+1})
\]

(1)

where \( 4K \) is the number of atoms, \( \hat{c}_p^{\dagger} \) and \( \hat{c}_p \) are the creation and annihilation operators for the function \( \chi_p \), and \( \epsilon_p \) and \( -t_{p,p+1} \) are on-site energies and hopping integrals, respectively. The matrix elements of the position operator are given by \( \langle \chi_n|\hat{z}|\chi_m\rangle = \delta_{n,m} z_n \) with \( z_p \) being the position of the \( p \)th atom. For convenience, the atoms are taken to be equally spaced, \( z_p = \frac{a}{2}[p - \frac{1}{2}] \), with \( p = -2K + 1, \ldots, 2K \) being odd (even) for the A (B) atoms, and \( \frac{a}{2} \) being the nearest-neighbor distance. Assuming one electron per atom it is straightforward to evaluate the atomic charges and the electronic polarization, \( P \) (dipole moment per A-B unit) as a function of the number of A-B units, \( 2K \). As an example (using arbitrary units for length and energy and setting the electronic charge equal to +1) for \( a = 2.0 \), alternating on-site energies \( \epsilon_p = \pm 0.5 \equiv \pm \epsilon_0 \), and hopping integrals \( t_+ = -2.2 \), \( t_- = -1.8 \), we find that the polarization is converged to a value \( P = 0.58125 \) for \( K > 13 \).
while the charges on the central atoms are $Q(A) = 0.74413$, $Q(B) = 1.25587$. The latter result in a contribution $P_c = P - \frac{2}{7}[Q(B) - Q(A)] = 0.32538$ to the polarization due to accumulation of charge at the chain ends. We may think of $P_c$ as an intercellular charge flow term. The existence of a substantial intercellular charge flow term is remarkably robust to variations in the model. Thus, including next-nearest-neighbor interactions, modifying the matrix elements at the chain ends or altering $\langle \chi_n | \hat{z} | \chi_m \rangle$ in realistic ways often changes the total dipole moment, but not the polarization, of sufficiently long chains. The effect of varying terminal (on-site and/or hopping) matrix elements is illustrated in Fig. 1. The figure shows that altering the chain ends changes the charges on the ends (upper part) and the dipole moment (lower part) but neither the polarization (slope of dipole-moment curve) nor the charges in the central region are affected. The right hand panel of the lower part shows that the polarization can vary for small chains (see, particularly, curve f).

The fact that one may calculate the polarization by studying only the central cells has been shown previously by Vanderbilt and King-Smith [9]. However, this does not imply that different terminating groups, which lead to different charge accumulation at the chain ends, give the same polarization because there is a contribution due to intercellular charge flow that could change. Thus, this is a generalization of the Vanderbilt and King-Smith result, which is consistent with the known near-sightedness [11] of the single-particle density matrix. It has obvious implications for the design of donor-acceptor, or push-pull, systems and is valid provided the chain is sufficiently long.

Even for an unsubstituted chain where the ends are connected so that no charge can accumulate there is an important contribution to the polarization that arises from the intercellular charge flow. We now turn to that case and consider a ring of $2K$ identical AB unit cells. Application of periodic boundary conditions leads to the general expression for the eigenfunctions

$$\psi^k_n(\vec{r}) = u^k_n(\vec{r})e^{ikz} = \frac{1}{\sqrt{2K}} \sum_{m=-K+1}^{K} e^{ikam} \sum_{p=1}^{N_b} c^k_{pm} \chi_{pm}(\vec{r}), \quad (2)$$

with $n$ being a band index, $\chi_{pm}$ the $p$th basis function of the $m$th unit cell, and $N_b$ the number of basis functions per cell. In our Hückel model, $n = 1 \ (n = 2)$ for the occupied (empty) band, and $p = 1 \ (p = 2)$ indicates the function on the A (B) atom. For any given set of parameters and sufficiently long chains the electronic charges, $Q(A)$ and $Q(B)$, turn out to be identical to those at the center of the open-ended chain of the same length. Thus, for either chain, the same intracellular polarization $\frac{2}{7}[Q(B) - Q(A)]$ is obtained. This means that the $P_c$ contribution must be accounted for in some other way. For the ring we can readily identify that contribution by considering Blount’s expression for
the polarization in the limit $K \to \infty$:

$$P = \frac{ia}{\pi} \sum_n \int \langle u_n^k | \frac{\partial}{\partial k} u_n^k \rangle dk,$$

where the $n$ summation is over the (doubly) occupied bands. Using Eq. (2) it is easy to show (cf. [12]) that

$$P = \frac{1}{\pi} \sum_n \sum_{m=-N}^N \int e^{ikma} \sum_{pq} c_{qm}^{k*} \left( \langle \chi_{pq} | z - ma | \chi_{pm} \rangle + i \langle \chi_{pq} | \chi_{pm} \rangle \frac{d}{dk} \right) c_{pm}^k dk.$$

(4)

With a finite $2K$-point-mesh approximation for the integral one can verify that the first term on the rhs of Eq. (4) yields the intracellular polarization. This leaves the second term as the periodic cyclic chain analogue of the intercellular charge flow contribution described above in connection with the open chain.

If one is interested in long open-ended chains it is usually advantageous computationally to assume that the chain is infinite and periodic. A number of different proposals have been advanced for calculating the polarization of infinite periodic chains using finite $k$ mesh methods. In order to compare these approaches we follow the treatment of Blount [1], based on the relation

$$z\psi_n^k(\vec{r}) = ie^{ikz} \frac{\partial}{\partial k} e^{-ikz}\psi_n^k(\vec{r}) - i \frac{\partial}{\partial k}\psi_n^k(\vec{r}),$$

(5)

to obtain the effect of the coordinate $z$ acting on a single electron whose orbital, $\psi(\vec{r})$, is expanded in terms of Bloch waves

$$\psi(\vec{r}) = \sum_k \sum_n \psi_n^k(\vec{r}) f_n^k = \sum_k \sum_n e^{ikz} \psi_n^k(\vec{r}) f_n^k.$$

(6)

In fact, Blount [1] obtained Eq. (4) by using Eq. (5) on $\psi$ of Eq. (6). Here instead of a continuous $k$ we will use a finite $k$-mesh, which corresponds to assuming that the system possesses the periodicity of the Born von Kármán (BvK) zone containing $2K$ unit cells. Consequently, the analytical derivatives in Blount’s formulation will be replaced by numerical derivatives. In lowest order the numerical derivatives corresponding to the terms in Eq. (5) are:

$$\hat{\Delta}' \psi(\vec{r}) = \frac{1}{\Delta k} \sum_k \sum_n \left[ \psi_n^k(\vec{r}) f_n^k - \psi_n^{k-1}(\vec{r}) f_n^{k-1} \right]$$

$$\hat{\Delta}'' \psi(\vec{r}) = \frac{1}{\Delta k} \sum_k \sum_n e^{ikz} \left[ u_n^k(\vec{r}) f_n^k - u_n^{k-1}(\vec{r}) f_n^{k-1} \right]$$
\[ \hat{\Delta}_+ \psi(\vec{r}) = \frac{1}{\Delta_k} \sum_k \sum_n \left[ \psi_{n+1}^k(\vec{r}) f_n^{k+1} - \psi_n^k(\vec{r}) f_n^{k} \right] \]
\[ \hat{\Delta}_+'' \psi(\vec{r}) = \frac{1}{\Delta_k} \sum_k \sum_n e^{ikz} \left[ u_{n+1}^k(\vec{r}) f_n^{k+1} - u_n^k(\vec{r}) f_n^{k} \right] \]
\[ \hat{\Delta}_0 = \frac{1}{2}(\hat{\Delta}_- + \hat{\Delta}_+) \]
\[ \hat{\Delta}_0'' = \frac{1}{2}(\hat{\Delta}_-'' + \hat{\Delta}_+''), \]

(7)

with \( \Delta_k = \frac{\pi}{ak} \). By construction these expressions have the BvK periodicity and it follows that the lowest order finite-\( k \)-mesh analogues of \( \langle \psi | z | \psi \rangle \) are \( (\psi_n^{k+2\pi/a} = \psi_n^k) \):

\[ \langle \psi | (-i\hat{\Delta}_- + i\hat{\Delta}_-) | \psi \rangle = \langle \psi | \frac{i}{\Delta_k} (1 - e^{i\Delta k z}) | \psi \rangle = \frac{i}{\Delta_k} (1 - S^+) \]
\[ \langle \psi | (-i\hat{\Delta}_+ + i\hat{\Delta}_+) | \psi \rangle = \langle \psi | \frac{i}{\Delta_k} (e^{-i\Delta k z} - 1) | \psi \rangle = \frac{i}{\Delta_k} (S^- - 1) \]
\[ \langle \psi | (-i\hat{\Delta}_0 + i\hat{\Delta}_0) | \psi \rangle = \langle \psi | \frac{\sin(\Delta k z)}{\Delta k} | \psi \rangle = \frac{1}{2i\Delta_k} (S^+ - S^-), \]

(8)

where \( S^\pm = \langle \psi | e^{\pm i\Delta k z} | \psi \rangle \). If the spatial extent of \( \psi \) is much smaller than \( \frac{1}{\Delta k} \) (this can, e.g., be obtained by increasing the number of \( k \) points in an actual calculation), and assuming that \( \int_{BvK} |\hat{z}\psi(\vec{r})|^2 d\vec{r} \) exists (e.g. when \( \psi \) is a well-localized Wannier function), then we may make the approximation

\[ \langle \psi | i\frac{i}{\Delta k} e^{\pm i\Delta k z} | \psi \rangle \approx \frac{i}{\Delta_k} e^{\pm 2i\Delta k \langle \psi | z | \psi \rangle} \]

(9)

or

\[ \langle \psi | z | \psi \rangle \approx -\frac{i}{\Delta_k} \ln S^+ \approx -\frac{1}{\Delta_k} \text{Im} \ln S^+ \]
\[ \langle \psi | z | \psi \rangle \approx \frac{i}{\Delta_k} \ln S^- \approx \frac{1}{\Delta_k} \text{Im} \ln S^- \]
\[ \langle \psi | z | \psi \rangle \approx \frac{1}{\Delta_k} \text{Arcsin} \left[ \frac{1}{2i}(S^+ - S^-) \right]. \]

(10)

Here, the second equalities in the first two expressions have been obtained by removing the imaginary parts and, accordingly, requiring that \( \langle \psi | z | \psi \rangle \) is real. This result comes about automatically in the expressions based on the \( \hat{\Delta}_0 \) operators.

The treatment for \( N \) electrons is similar. In that case the one-electron Bloch waves are replaced by Slater determinants \( \Psi_i^k = \hat{A}[\psi_{i_1}^{k_1}(\vec{r}_1) \psi_{i_2}^{k_2}(\vec{r}_2) \cdots \psi_{i_N}^{k_N}(\vec{r}_N)] \), where \( \hat{A} \) is the antisymmetrizer, and Eq. (5) becomes
\[
\left( \sum_{n=1}^{N} z_n \right) \Psi_i^k = i \exp \left( i \sum_{n=1}^{N} k_n z_n \right) \left( \sum_{n=1}^{N} \frac{\partial}{\partial k_n} \right) \left( \exp \left( -i \sum_{n=1}^{N} k_n z_n \right) \Psi_i^k \right)
\]

\[-i \left( \sum_{n=1}^{N} \frac{\partial}{\partial k_n} \right) \Psi_i^k. \tag{11}\]

Then an arbitrary \(N\)-electron function can be written as the linear combination \(\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{\vec{k}} \sum_{\vec{i}} \Psi_{\vec{i}}^k(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) f_{\vec{i}}^k\) with the single-particle situation being a special case. The generalization of the quantities in Eq. (7) becomes

\[
\hat{\Delta}'_{-} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{\Delta_k} \sum_{\vec{i}} \sum_{\vec{k}} \left[ \Psi_{\vec{i}}^k(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) f_{\vec{i}}^k - \Psi_{\vec{i}}^{k-\Delta_k}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) f_{\vec{i}}^{k-\Delta_k} \right]
\]

\[
\hat{\Delta}''_{-} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{\Delta_k} \hat{A} \left\{ \sum_{\vec{i}} \sum_{\vec{k}} e^{i(k_1 z_1 + k_2 z_2 + \cdots + k_N z_N)} \right.
\]
\[
\times \left[ u_{i_1}^{k_1}(\vec{r}_1) u_{i_2}^{k_2}(\vec{r}_2) \cdots u_{i_N}^{k_N}(\vec{r}_N) f_{\vec{i}}^k - u_{i_1}^{k_1-1}(\vec{r}_1) u_{i_2}^{k_2-1}(\vec{r}_2) \cdots u_{i_N}^{k_N-1}(\vec{r}_N) f_{\vec{i}}^{k-\Delta_k} \right] \right\} \tag{12}\]

with analogous expressions for \(\hat{\Delta}'_{+}\) and \(\hat{\Delta}''_{+}\), \(\hat{\Delta}'_{0}\) and \(\hat{\Delta}''_{0}\). Hence, the generalization of Eq. (8) is

\[
\hat{\Delta}_{-} = -i \hat{\Delta}'_{-} + i \hat{\Delta}''_{-} = \frac{i}{\Delta_k} \left[ 1 - e^{i\Delta k (z_1 + z_2 + \cdots + z_N)} \right]
\]

\[
\hat{\Delta}_{+} = -i \hat{\Delta}'_{+} + i \hat{\Delta}''_{+} = \frac{i}{\Delta_k} \left[ e^{-i\Delta k (z_1 + z_2 + \cdots + z_N)} - 1 \right]
\]

\[
\hat{\Delta}_{0} = -i \hat{\Delta}'_{0} + i \hat{\Delta}''_{0} = \frac{1}{\Delta_k} \sin \left[ \Delta k (z_1 + z_2 + \cdots + z_N) \right]. \tag{13}\]

We will restrict ourselves to the case where there is a finite gap between occupied and unoccupied bands, assume no spin polarization (\(N\) is even), and use a single determinant wavefunction (Hartree-Fock or Kohn-Sham theory). Then

\[
\langle \Psi | \hat{\Delta}_{-} | \Psi \rangle = \frac{i}{\Delta_k} \left[ 1 - (\text{det} S^+)^2 \right]
\]

\[
\langle \Psi | \hat{\Delta}_{+} | \Psi \rangle = \frac{i}{\Delta_k} \left( (\text{det} S^-)^2 - 1 \right)
\]

\[
\langle \Psi | \hat{\Delta}_{0} | \Psi \rangle = \frac{1}{2i\Delta_k} \left[ (\text{det} S^+)^2 - (\text{det} S^-)^2 \right]. \tag{14}\]
where $S^{\pm}$ is the $N/2 \times N/2$ matrix containing the single-particle matrix elements $S^{\pm}_{(i,k),(j,l)} = \langle \psi^k_i | e^{\pm i \Delta k z} | \psi^l_j \rangle$. Assuming localized orbitals we may apply the analogue of Eq. (9), i.e.

$$\langle \Psi | \frac{i}{\Delta k} e^{\pm i \Delta k (z_1 + z_2 + \cdots + z_N)} | \Psi \rangle \sim \frac{i}{\Delta k} e^{\pm i \Delta k (\sum_{j=1}^{N} z_j)},$$  

(15)

and either of the first two equations in Eq. (14), in combination with Eq. (13), to arrive at the expression

$$P_R = -\frac{a}{\pi} \text{Im} \ln \det S^+ = \frac{a}{\pi} \text{Im} \ln \det S^-,$$

(16)

for the polarization. Note that $(S^+)^\dagger = S^-$. An essentially identical formula in terms of Bloch orbitals has been given by Resta [4]. We observe that Eq. (16) is based on a not too accurate finite-difference approximation to the derivative. A more accurate approximation is

$$P_0 = \frac{a}{2\pi} \text{Arcsin} \left[ \frac{1}{2i} (\det S^+)^2 - (\det S^-)^2 \right].$$

(17)

Despite this $P_R$ turns out to be more useful computationally. To see why we write

$$\det S^{\pm} = s \pm it,$$

(18)

whereby

$$P_R = -\frac{a}{\pi} \text{Arctan} \left( \frac{t}{s} \right),$$

$$P_0 = \frac{a}{2\pi} \text{Arcsin}(2st).$$

(19)

As $K \to \infty$, $s^2 + t^2 \to 1$, while $|s|, |t| < 1$ are increasing functions of $K$. Accordingly, as our numerical results below confirm, $P_R$ converges faster than $P_0$ as a function of $K$. On the other hand, $P_0$ can be valuable analytically; indeed, it motivated our choice for the operator defined in Eq. (23) below.

The value of $\det S^{\pm}$ will not be altered by an arbitrary unitary transformation of the single determinant orbitals. So, instead of localized orbitals we may use the occupied Bloch waves from which these orbitals are obtained. Then, the matrix elements of $S^{\pm}$ are non-zero only for pairs of Bloch waves whose $k$ values differ by $\Delta k \ (\text{modulus} \ \frac{2\pi}{a})$. As a result $S^{\pm}$ can be written as consisting
of $2K \times 2K$ square blocks, each of dimension $B = \frac{N}{4K}$ (the number of doubly-occupied bands) with non-zero elements only in the set of blocks lying one stripe above and one stripe below the main diagonal.

Given that the Bloch functions are differentiable with respect to $k$ as discussed by Blount we obtain for small $\Delta k$

$$\ln(\det S^\pm)^2 \simeq \mp 2\Delta k \sum_{k=1}^{2K} \sum_{n=1}^{B} \langle u_n^k | \frac{\partial}{\partial k} u_n^k \rangle.$$  \hspace{1cm} (20)

Inserting this into the rhs of Eq. (16) yields another formula for the polarization

$$P_{KSV} = \frac{iK}{R} \sum_{k=1}^{2K} \sum_{n=1}^{B} \langle u_n^k | \frac{\partial}{\partial k} u_n^k \rangle,$$ \hspace{1cm} (21)

which is the 1D discretized Berry phase expression [9] used in the modern theory of polarization.

For the treatment of core orbitals (or those of non-interacting periodically repeated molecules) we suppose that the orbitals are strongly localized so that $\langle \psi_{p_1}(\vec{r} - \vec{R}_{n_1})|e^{\pm i\Delta kz}|\psi_{p_2}(\vec{r} - \vec{R}_{n_2}) \rangle$ vanishes unless the units $n_1$ and $n_2$, where the functions are centered, are identical. In that case we may write for orbitals of the same unit

$$\langle \psi_{p_1}|e^{\pm i\Delta kz}|\psi_{p_2} \rangle \simeq \delta_{p_1,p_2} e^{\pm i\Delta k z_{p_1,p_2}} \pm i\Delta k \langle \psi_{p_1}|z - z_{p_1,p_2}|\psi_{p_2} \rangle$$

$$+ \frac{(i\Delta k)^2}{2} \langle \psi_{p_1}|(z - z_{p_1,p_2})^2|\psi_{p_2} \rangle + \cdots$$ \hspace{1cm} (22)

with $z_{p_1,p_2}$ being the ‘center’ of the $p_1$th and $p_2$th orbital. Therefore, the ‘traditional’ contribution to the polarization from these orbitals, i.e., $\sum_p \langle \psi_p |z|\psi_p \rangle$, is obtained only in the case where all terms but the first one on the rhs of Eq. (22) are negligible (e.g. in the limit $\Delta k \to 0$).

So far we have presented an internally consistent approach for how to calculate the polarization in an infinite, periodic chain when basing the discussion on a generalization of Blount’s work to the case of a finite BvK zone. We have arrived at an expression involving the expectation values for $N$-body operators, i.e., the $S^\pm$ matrices. This has been taken as a proof that the polarization is a many-body phenomenon [6,7]. However, the polarization can also be written in terms of the single-particle operator...
\[
\hat{P} = \frac{1}{2i\Delta k} \sum_{m=1}^{N} \sum_{k'} \sum_{n'} \left[ e^{i\Delta k z_m} |\psi_n^{k'-1}(\vec{r}_m)\rangle \langle \psi_{n'}^{k'}(\vec{r}_m)| - e^{-i\Delta k z_m} |\psi_n^{k'+1}(\vec{r}_m)\rangle \langle \psi_{n'}^{k'}(\vec{r}_m)| \right].
\] (23)

It is straightforward to show that the expectation value of this operator gives \(P_0\) in the limit \(\Delta k \to 0\).

In order to explore our ideas further, the Hückel-like model described above was used to evaluate the various polarization expressions we have presented. For our purposes it is necessary to have matrix elements of \(z\) and \(e^{\pm i\Delta k z}\) that are defined consistently. Hence, we calculated the matrix elements in both cases analytically assuming piecewise constant basis functions of adjustable width, \(w\). For simplicity we also assumed that \(w < \frac{a}{2}\), whereby the results become independent of \(w\). Other more realistic functions are possible, of course, but the above choice is sufficient to make the desired comparisons.

In Table 1 we show some typical results for the various choices of \(P\) obtained using BvK periodic boundary conditions. The finite chain value determined from the increment \(\Delta D = \frac{1}{2} [D(2K + 2) - D(2K)]\), where \(D\) is the dipole moment, is also presented for comparison. In order to interpret polarization values the reader should recall that \(P\) is determined only up to an arbitrary multiple of the unit cell length [cf. Eqs. (16) and (17)], which in this case is 2.0. Bearing this in mind, the table shows that \(\Delta D\) agrees very well with the polarization of the infinite system given by \(P_R\). Indeed, the finite chain result converges more rapidly to the infinite \(K\) limit. The sawtooth approximation (denoted \(P_{st}\) in the table) is calculated using periodic boundary conditions with \(z\) replaced by a piecewise linear function having the BvK periodicity. Note that \(P_{st}\) gives the correct value only when the system consists of purely non-interacting units (last case in table). Since \(\sin(\alpha) = \sin(\pi - \alpha)\) it is not possible to discriminate between \(P_0\) and \(\frac{a}{2} - P_0\) (cf. the first case in the table). If that is taken into account, we see that \(P_{KSV}, P_R,\) and \(P_0\) all give similar results, although the latter converges much slower, and the former much faster, than the others.

In conclusion we have provided a unified picture of electronic polarization in extended quasilinear chains based primarily on the finite \(k\)-mesh analogue of Blount’s treatment for infinite periodic systems. Separate intracellular and intercellular contributions are identified and compared between closed and open chains. It is shown that neither component is affected by substitution at the end of an open chain, as occurs in a push-pull compound. On the other hand, the traditional sawtooth formulation for infinite closed chains fails to account for the intercellular charge flow term. Several different expressions for the electronic polarization are systematically generated from the same starting point, including those related to the so-called modern theory of polarization.
From the same perspective we obtain an alternative single particle operator, which yields the polarization as its expectation value. Hückel-type calculations are carried out to illustrate all of these points and to assess the convergence properties of the various polarization formulas as the \( \kappa \)-mesh spacing decreases to zero.

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Table 1
Results of model calculations with the Hückel model. The lattice constant equals $a = 2$. All other parameter values are given in the table.

| $\epsilon_0$ | $t_+$ | $t_-$ | $K$ | $P_{st}$  | $P_R$    | $P_{KSV}$ | $P_0$  | $\Delta D$ |
|------------|------|------|----|---------|---------|---------|-------|-----------|
| 0.5        | 2.2  | 1.8  | 20 | 0.25587 | -1.41859| -1.41745| 0.29410| 0.58125   |
|            | 200  |      |    | 0.25587 | -1.41875| -1.41875| 0.39798| "         |
|            | 2000 |      |    | 0.25587 | -1.41875| -1.41875| 0.41643| "         |
|            | 20000|      |    | 0.25587| -1.41875| -1.41875| 0.41852| "         |
| 0.5        | 2.5  | 1.5  | 20 | 0.21337 | -1.68291| -1.68305| 0.26857| 0.31695   |
|            | 200  |      |    | 0.21337 | -1.68305| -1.68305| 0.31134| "         |
|            | 2000 |      |    | 0.21337| -1.68305| -1.68305| 0.31638| "         |
|            | 20000|      |    | 0.21337| -1.68305| -1.68305| 0.31690| "         |
| 0.5        | 1.5  | 1.5  | 20 | 0.33562 | -1.00000| -3.00000| 0.00000| 1.00000   |
|            | 200  |      |    | 0.33562 | -1.00000| -3.00000| 0.00000| "         |
|            | 2000 |      |    | 0.33562| -1.00000| -3.00000| 0.00000| "         |
|            | 20000|      |    | 0.33562| -1.00000| -3.00000| 0.00000| "         |
| 0.0        | 2.5  | 1.5  | 20 | 0.00000| -2.00000| -2.00000| 0.00000| 0.00000   |
|            | 200  |      |    | 0.00000| -2.00000| -2.00000| 0.00000| "         |
|            | 2000 |      |    | 0.00000| -2.00000| -2.00000| 0.00000| "         |
|            | 20000|      |    | 0.00000| -2.00000| -2.00000| 0.00000| "         |
| 0.5        | 2.0  | 0.0  | 20 | 0.24254| -1.75735| -1.75746| 0.22586| 0.24254   |
|            | 200  |      |    | 0.24254| -1.75746| -1.75746| 0.24078| "         |
|            | 2000 |      |    | 0.24254| -1.75746| -1.75746| 0.24236| "         |
|            | 20000|      |    | 0.24254| -1.75746| -1.75746| 0.24252| "         |
Fig. 1. Upper part: Distribution of the atomic charges as a function of atom index for a finite chain with 80 atoms for different cases of the matrix elements for the terminating atoms, i.e., the on-site energies for the first (last) atom have been modified as $\epsilon_0 \rightarrow \epsilon_0 + \Delta \epsilon_l (-\epsilon_0 \rightarrow -\epsilon_0 + \Delta \epsilon_r)$, and the hopping integrals between the first (last) two atoms according to $-t_+ \rightarrow -t_+ + \Delta t_l (-t_+ \rightarrow -t_+ + \Delta t_r)$. Lower part: The dipole moment for the same cases but as a function of chain length. Here, ‘sawtooth’ corresponds to the dipole moment for a ring system when using the sawtooth approximation, and the right panel shows a blow-up of the low-$K$ part. The curves marked $a, b, c, d, e,$ and $f$ (in the lower panels these labels are listed in the same order as the curves appear) correspond to the following modifications: $(\Delta \epsilon_l, \Delta \epsilon_r, \Delta t_l, \Delta t_r) = (0, 0, 0, 0), (1.0, 0, 0, 0), (0, 1.0, 0, 0), (0, 0, -1.0, 0), (0, 0, 0, -1.0), \text{and} (1.0, -1.0, -1.0, 1.0)$, respectively.