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Analysis of vector potential approach for calculating linear and nonlinear responses of infinite periodic systems to a finite static external electric field

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The vector potential approach for calculating the polarization of an infinite periodic system induced by a uniform finite electrostatic field is described in detail. It is demonstrated that the resulting secular equation can also be obtained from one particular version of the modern theory of polarization. A key element of this computationally advantageous crystal orbital treatment is an efficient procedure for smoothing the occupied orbitals as a function of the wave vector *k*. Based on a carefully constructed model polymer Hamiltonian, we find good convergence of the self-consistent field solutions even when many *k* points are required for accuracy, and even at fields well beyond the estimated threshold for Zener tunneling. Characteristic signals for the onset of breakdown due to Zener tunneling are established. An analytical expression for the forces is obtained and used to determine geometry relaxation due to the field. The validity and accuracy of the approach are demonstrated through comparison with results for long finite chains. Finally, some interesting implications for donor-acceptor substitution at the chain ends are discussed.

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I. INTRODUCTION

The response to external electric and magnetic fields provides a fundamental tool for studying and altering the properties of materials with numerous attendant applications. An important ingredient for effectively utilizing this tool is the ability to relate the properties to electronic structure through computations. Such computations depend, of course, on having an appropriate theoretical basis along with suitable algorithms for implementing the theory. In the case of finite systems, such as ordinary atoms and molecules, a great deal of progress has been made in this regard and many aspects are very well established.

Although all systems are finite, in many cases it is convenient to treat them as being infinite and periodic. These cases include polymers, chain compounds, surfaces, films, and crystals. For these systems, the theoretical developments are in a much more primitive state. As far as the response to spatially uniform electric fields is concerned (the case considered here), that is because the scalar interaction potential, normally used in atomic and molecular calculations, is proportional to the quantum-mechanical operator $\vec{r}$ (i.e., the electronic position), which is nonperiodic and unbounded from below.

A number of different methods have been suggested for dealing with this situation. The most straightforward is to study finite systems of increasing size and, then, extrapolate to the infinite-size limit. At the first-principles level, this approach is prohibitively CPU demanding for three-dimensional (3D) solids, but it is manageable (and has been implemented) for quasilinear polymers (see, e.g., Ref. 1). The key issue is how to reliably extrapolate when the functional dependence of the property on chain length is unknown.[2–4]

A different approach, standard in solid-state physics, is to adopt Born–von-Kármán (BvK) periodic boundary conditions in order to describe the infinite-system limit. In this way, there is no surface. By construction, any computed property is defined as "bulk." At the same time, $\vec{r}$ may be approximated as a sawtooth function with the periodicity of the BvK zone.[5–8] Despite some successes, we have shown in an earlier work[9] that the sawtooth method does not, in general, correctly account for the polarization. It is missing a contribution that may be expressed as being due to a flow of electronic charge throughout the system. This contribution becomes important when there is substantial electron delocalization. Alternatively, one may write the field-free crystal orbitals in Bloch form so that, when operated upon by $\vec{r}$, the result can be separated into a sum of two terms, one of which possesses the lattice periodicity, while the other does not.[10–14] Despite initial questions with regard to the particular partitioning used,[15] it has since been demonstrated (see below) that the nonperiodic term, as originally defined, can be discarded. Recently, this procedure has been implemented for linear polarizabilities of one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) systems.[13]

Within the past 10–15 years, another method, often referred to as the "modern theory of polarization" (MTP), has become popular, particularly for periodic 3D solids.[16–18] The MTP is based on a discretized Berry phase treatment and has been applied to calculate the static polarization (i.e., permanent dipole moment per unit volume) and linear polarizability of many 3D materials, most notably piezoelectrics and ferroelectrics.[19–22] The method has been extended to static finite fields,[23–29] and a formulation for the treatment of time-dependent fields has been given as well.[30] However, an approach based on solving a standard secular equation has, to our knowledge, not been presented.

A completely different methodology has been adopted by Kirtman and co-workers.[31,32] Instead of dealing with the scalar potential or (explicitly) with the Berry phase, these authors have developed a vector potential approach (VPA) based on a suggestion made initially by Genkin and Mednis (GM).[33] Taken together with the prescription for the polarization operator given by GM, as well as by Blount,[34] this approach has the virtue of immediately satisfying the periodicity requirement and of introducing frequency dependence in a straightforward manner while still being applicable to static fields. It also, incidentally, provides a rigorous mathematical justification[31] for the (periodic/nonperiodic) partitioning technique mentioned above. The VPA has been successfully used to determine both linear and nonlinear polarizabilities[32,35–38] although calculations have been limited to the pure electronic response of quasi-one-dimensional (quasi-1D) systems.

The most important advantage of the VPA stems from the fact that it yields a Schrödinger-type crystal orbital equation. This equation differs fundamentally from the one that occurs for molecules because of an additional charge flow (or current) term.[31] Nevertheless, with suitable modifications, one can utilize the numerous solution techniques that have proved so valuable in the development of computational quantum chemistry. The Berry phase does not appear explicitly nor is discretization required.

In order to determine field-induced geometric phase transitions, vibronic nonlinear optical properties, etc., the ability to obtain not only the electronic response to a finite field, but also the structural and/or vibrational response is crucial. Nonetheless, this subject has not yet been thoroughly considered within the VPA. As noted above, there is a MTP treatment of finite fields, but it is at an early stage with some admitted computational difficulties in some cases.[23] On the other hand, a preliminary study[39] indicates that these difficulties are avoided in the VPA by adopting (appropriately modified) conventional *ab initio* quantum-chemistry procedures. In addition to Ref. 39, an abbreviated account of this work was given in Ref. 9.

The purpose of the current paper is to present in detail, and to analyze, our VPA method for calculating (non)linear electronic and structural responses of infinite periodic systems to finite (static) electric fields. It will be argued that our approach is superior to others that have been proposed. The electronic single-particle equations that we utilize have certain nonstandard features, making it very important to develop new methods for solving them. For both finite and infinite periodic systems, there are no bound states in the presence of an electrostatic field. This leads to convergence issues in describing the resonance states, which must be addressed for any computational procedure. These issues are examined herein through direct calculations. The treatment presented here will focus on quasi-1D chains and neglect spin polarization, although the basic ideas are readily transferable to 2D and 3D systems and/or to the spin-polarized case.

This paper is organized as follows. In Sec. II, we present the VPA Schrödinger-like equation for an infinite, periodic system in an external electrostatic field and demonstrate that the same result can be derived from one particular version of the MTP. We also show that our formulation has appealing features in comparison with current MTP-based treatments. In Sec. III, an efficient and accurate self-consistent field (SCF) method for solving the VPA-based single-particle equation is presented. Based on model calculations, we examine the convergence behavior of the SCF solutions as a function of the number of k points and the field in Sec. IV. In addition, this section contains a discussion of the band structure and threshold for Zener tunneling as well as calculations of the linear and nonlinear electronic responses. Analytical derivatives for field-dependent forces are reported in Sec. V along with their application to geometry relaxation induced by a finite field. In Sec. VI, we discuss some implications of our analysis for long, but finite, push-pull chains. Finally, Sec. VII contains a summary of our results along with some directions for future investigation.

Throughout the paper we shall set the electronic charge equal to -1 as well as $\hbar=1$.

II. FUNDAMENTAL EQUATIONS

In this section, we present the VPA single-particle Schrödinger-type equation for the electrons of an infinite, periodic system in an external electrostatic field. Although this equation is not a “normal” eigenvalue relation, it is recast as such. Then, a comparison is made with the scalar potential approach, especially with the variational expressions that can be derived from the several alternative formulations that have been proposed. We show that this leads either to the VPA equation or to some other relation which is less advantageous from a computational point of view.

A. Vector potential approach

Depending on the choice of gauge, an external electric field can be included either via the vector potential $\vec{A}(t)$ or the scalar potential $V_F(t)$ (note that the field may be time dependent). In this section, the first case is considered, and in the next section, the second one. We study particularly a periodic quasi-1D system that lies parallel to the z axis. In the absence of an external electric field, the orbitals of interest are typically written as Bloch waves,

$$\psi(\vec{r}) = \psi_j(k,\vec{r}) = e^{ikz}u_j(k,\vec{r}), \tag{1}$$

with j being a band index and $u_j(k,\vec{r})$ a periodic unit cell function. In a typical calculation, a finite set of K equidistant k points in the interval $\left[-\frac{\pi}{a};\frac{\pi}{a}\right]$ is used. Here, $a=|\vec{a}|$ is the lattice constant, and the k spacing is

$$\Delta k = \frac{2\pi}{Ka}. \tag{2}$$

Finally, we consider only systems with a gap between filled and empty bands.

Within either Hartree-Fock or Kohn-Sham theory, the Slater determinant wave function Ψ consists of $2N\times K$ occupied spin orbitals, with $2N$ being the number of electrons per unit. As is well known, the jth orbital can be constructed from atom-centered basis functions, $\{\chi_{mp}\}$ $[\chi_{mp}(\vec{r})$ is the pth basis function of the mth unit cell$]$, in two equivalent ways

$$\psi_j(\vec{r}) = \sum_{mp} C_{mpj}\chi_{mp}(\vec{r}),$$

$$\psi_j(k,\vec{r}) = \sum_{p} C_{pj}(k)\chi_p(k,\vec{r}). \tag{3}$$

In the second identity, we have used the formulation in which $\chi_p(k,\vec{r})$ is a Bloch wave constructed from the K corresponding basis functions of the different units, i.e.,

$$\chi_p(k,\vec{r}) = \frac{1}{\sqrt{K}}\sum_m e^{ikam}\chi_{mp}(\vec{r}). \tag{4}$$

In the presence of an external electric field, the single-particle momentum operator is replaced by $\hat{\vec{p}}-\frac{1}{c}\vec{A}(t)$ in the VPA. As shown by Kirtman *et al.*,[31] using the second expansion of Eq. (3) in the time-dependent single-particle Hartree-Fock (or Kohn-Sham) equation

$$\left(\hat{F} - i\frac{\partial}{\partial t}\right)\psi_{j_1}(k,\vec{r},t) = \sum_{j_2}\epsilon_{j_2 j_1}(k)\psi_{j_2}(k,\vec{r},t) \tag{5}$$

leads to

$$\underline{\underline{F}}(k,t)\cdot\underline{\underline{C}}(k,t) - V_F(t)\cdot\left[\underline{\underline{M}}(k)\cdot\underline{\underline{C}}(k,t) + i\underline{\underline{S}}(k)\frac{\partial}{\partial k}\underline{\underline{C}}(k,t)\right] - i\underline{\underline{S}}(k)\frac{\partial}{\partial t}\underline{\underline{C}}(k,t) = \underline{\underline{S}}(k)\cdot\underline{\underline{C}}(k,t)\cdot\underline{\underline{\epsilon}}(k,t). \tag{6}$$

$\underline{\underline{C}}$ is the matrix containing the orbital expansion coefficients. Since the field $V_F(t)$ is time dependent, so are the orbital expansion coefficients, the Fock matrix, and the matrix of Lagrange multipliers, $\underline{\underline{\epsilon}}(k,t)$, that enforce the orthonormality constraints

$$\langle\psi_{j_1}(k,\vec{r},t)|\psi_{j_2}(k,\vec{r},t)\rangle = \delta_{j_1,j_2}. \tag{7}$$

Finally,

$$S_{qp}(k) = \sum_l e^{ikal}\langle\chi_{0q}|\chi_{lp}\rangle,$$

$$M_{qp}(k) = \sum_l e^{ikal}\langle\chi_{0q}|z-la|\chi_{lp}\rangle = \sum_l e^{-ikal}\langle\chi_{lq}|z|\chi_{0p}\rangle,$$

$$F_{qp}(k,t) = \sum_l e^{ikal}\langle\chi_{0q}|\hat{F}(t)|\chi_{lp}\rangle = h_{qp}(k,t) + \sum_{k_1}\sum_{q_1 p_1} P_{q_1 p_1}(k_1,t)v_{q_1 q p_1 p}(k_1,k) \tag{8}$$

are the overlap, unit cell dipole, and Fock matrix elements, respectively. We have written the total field-free electronic Hamiltonian here as a sum of one- and two-electron terms,

$$\hat{H}(t) = \sum_i \hat{h}(\vec{r}_i,t) + \frac{1}{2}\sum_{i\neq j} v(\vec{r}_i,\vec{r}_j), \tag{9}$$

and have introduced the density matrices

$$P_{qp}(k,t) = \sum_j C^*_{qj}(k,t)C_{pj}(k,t). \tag{10}$$

Moreover,

$$h_{qp}(k,t) = \sum_l e^{ikal}\langle\chi_{0q}|\hat{h}(t)|\chi_{lp}\rangle \tag{11}$$

and

$$v_{q_1 q_2 p_1 p_2}(k_1,k_2) = \frac{1}{K}\sum_{l_1,l_2,m_2} e^{ia(k_1 l_1 + k_2 l_2 - k_2 m_2)} \times(\langle\chi_{0q_1}\chi_{m_2 q_2}|v|\chi_{l_1 p_1}\chi_{l_2 p_2}\rangle - \langle\chi_{0q_1}\chi_{m_2 q_2}|v|\chi_{l_2 p_2}\chi_{l_1 p_1}\rangle). \tag{12}$$

For the special case of static fields, there is no time dependence, i.e., $V_F(t)=E_{\mathrm{dc}}$ is a constant. In addition, one may choose the Lagrange multipliers so that only diagonal elements are nonvanishing. Then, Eq. (6) becomes

$$\left\{\underline{\underline{F}}(k) - E_{\mathrm{dc}}\cdot\left[\underline{\underline{M}}(k) + i\underline{\underline{S}}(k)\frac{\partial}{\partial k}\right]\right\}\cdot\underline{C}_j(k) = \epsilon_j(k)\cdot\underline{\underline{S}}(k)\cdot\underline{C}_j(k), \tag{13}$$

where $\underline{C}_j(k)$ is the jth column of $\underline{\underline{C}}(k)$. Due to the $\frac{\partial}{\partial k}$ term, this equation is not a standard matrix-eigenvalue problem. However, it can be recast in the standard form by multiplying the $\frac{\partial}{\partial k}$ term on the right-hand side with $\underline{\underline{1}}=\underline{\underline{C}}^{\dagger}(k)\cdot\underline{\underline{S}}(k)\cdot\underline{\underline{C}}(k)$, which gives

$$\underline{\underline{S}}(k)\frac{\partial}{\partial k}\underline{\underline{C}}(k) = \left[\underline{\underline{S}}(k)\left(\frac{\partial}{\partial k}\underline{\underline{C}}(k)\right)\underline{\underline{C}}^{\dagger}(k)\underline{\underline{S}}(k)\right]\underline{\underline{C}}(k). \tag{14}$$

Equation (13) then takes the form

$$\left\{\underline{\underline{F}}(k) - E_{\mathrm{dc}}\cdot\left[\underline{\underline{M}}(k) + i\underline{\underline{S}}(k)\cdot\left(\frac{\partial}{\partial k}\underline{\underline{C}}(k)\right)\cdot\underline{\underline{C}}^{\dagger}(k)\cdot\underline{\underline{S}}(k)\right]\right\}\cdot\underline{C}_j(k) = \epsilon_j(k)\cdot\underline{\underline{S}}(k)\cdot\underline{C}_j(k). \tag{15}$$

It is easy to show that the effective Hamiltonian (in curly brackets) remains Hermitian. As usual, one must solve for the eigenvectors self-consistently.

Beyond resulting in a conventional eigenvalue equation, the additional advantages of this approach include the fact that k remains a good quantum number and, accordingly, there is a favorable scaling with the number of k points. At the same time, the matrix in curly brackets on the left-hand side can be handled in a relatively simple manner as we will see.

B. Scalar potential approach

In this section, we discuss variational approaches for including the external electrostatic field by means of the scalar potential which, for a single electron, is $-E_F\cdot z$ (the electrostatic field is along the z direction). Ultimately, we show that the most attractive numerical procedure is identical to the above VPA formulation.

When an electrostatic field is present, we seek the minimum of

$$G = \langle\Psi|\hat{H}|\Psi\rangle - E_{\rm dc}\cdot K\cdot P_e - \sum_{j_1j_2}\lambda_{j_1j_2}(\langle\psi_{j_1}|\psi_{j_2}\rangle - \delta_{j_1,j_2}). \tag{16}$$

There are at least three different ways of obtaining the electronic polarization, P_e. The equation that results from minimizing G depends on the particular choice.

According to the MTP (see, e.g., Ref. 9),

$$P_e \equiv \frac{1}{K}\left\langle \Psi \left| \sum_{m=1}^{2NK} z_m \right| \Psi \right\rangle \tag{17}$$

can be approximated through

$$P_{\rm R} = \frac{a}{\pi}\,\mathrm{Im}\ln\det\underline{\underline{S}}^{+} = -\frac{a}{\pi}\,\mathrm{Im}\ln\det\underline{\underline{S}}^{-}. \tag{18}$$

P_R is the original form proposed by King-Smith and Vanderbilt[16] and Resta.[17,18] In Eq. (18), the $(NK)\times(NK)\underline{\underline{S}}^{\pm}$ matrices contain elements of the type

$$S^{\pm}_{j_1j_2} = \langle\psi_{j_1}|e^{\pm i\Delta kz}|\psi_{j_2}\rangle. \tag{19}$$

Here, ψ_j is the jth orbital for the system of interest as represented, for instance, in Eq. (3). When the Bloch functions of the latter equation are used, $\langle\psi_{j_1}(k_1)|e^{\pm i\Delta kz}|\psi_{j_2}(k_2)\rangle \neq 0$ only for $k_1 = k_2 \pm \Delta k$, i.e., the polarization is nondiagonal in k.

Alternatively, one may consider an expression due to King-Smith and Vanderbilt (KSV),[16] which can be obtained from P_R by keeping the lowest-order term in Δk,

$$P_{\rm KSV} = \frac{2i}{K}\sum_{k=1}^{K}\sum_{j=1}^{N}\left\langle u_j(k)\left|\frac{\partial}{\partial k}\right|u_j(k)\right\rangle. \tag{20}$$

Finally, it can be shown[34] that Eq. (20) is equivalent to

$$P_w = \frac{2}{K}\sum_{p=1}^{K}\sum_{j=1}^{N}\langle w_{jp}|z|w_{jp}\rangle, \tag{21}$$

where w_{jp} is the pth Wannier function for the jth band.

Starting with some initial guess (this might, for example, be the field-free orbitals), one could minimize G of Eq. (16) directly. Such an approach was taken by Souza *et al.*,[23] who used successive 2×2 orbital rotations and $P_e = P_{\rm KSV}$. However, this procedure is computationally extensive and not particularly stable. Umari and Pasquarello[24] as well as Stengel and Spaldin[27] used a similar direct approach based on $P_e = P_w$ in combination with plane waves and a Car-Parrinello optimization. Here, we consider, instead, a more conventional quantum-chemistry formulation that can be obtained by varying the orbital expansion coefficients to yield, ultimately, a secular equation.

In applying the variational approach to P_R, we note [cf. Eq. (19)] that k is not a good quantum number. Thus, the resulting secular equation in matrix form,

$$(\underline{\underline{F}} - E_{\rm dc}\cdot\underline{\underline{R}})\cdot\underline{C_j} = \epsilon_j\cdot\underline{\underline{S}}\cdot\underline{C_j}, \tag{22}$$

will have the dimension of the BvK zone (NK). Without working out the details, it is evident that differentiation of $\det\underline{\underline{S}}^{\pm}$ will lead to an $\underline{\underline{R}}$ matrix that depends on the coefficients $\{C_{mpj}\}$ in a highly nonlinear manner. Moreover, since Eq. (22) has the dimension of the BvK zone, the numerical task of calculating the orbital energies and expansion coefficients will scale unfavorably with the number of k points. Thus, we discard this approach and turn now to the remaining ways of determining the electronic polarization.

Using the second expression in Eq. (3), together with Eq. (1), leads to

$$\begin{aligned} K\cdot P_{\rm KSV} &= 2i\sum_k\sum_j\left\langle\psi_j(k)\left|e^{ikz}\frac{\partial}{\partial k}e^{-ikz}\right|\psi_j(k)\right\rangle \\ &= 2\sum_k\sum_j\sum_{pq}\Bigg[C^*_{pj}(k)C_{qj}(k)M_{pq}(k) \\ &\quad + iC^*_{pj}(k)\frac{\partial C_{qj}(k)}{\partial k}S_{pq}(k)\Bigg] \equiv K\cdot(P_1+P_2), \end{aligned} \tag{23}$$

where we have split $P_{\rm KSV}$ into a charge term (P_1) and a current term (P_2), which will be useful for interpretive purposes later on. It is easily shown that, with this expression for the polarization in Eq. (16), the secular equation obtained is identical to the VPA equation [i.e., Eq. (13)].

With P_w of Eq. (21), one may take one of two different approaches. One possibility is to write the Wannier functions in terms of Bloch functions

$$w_{jp}(\vec{r}) = \frac{1}{\sqrt{K}}\sum_k e^{-ikap}e^{i\phi_j(k)}\psi_j(k,\vec{r}) \tag{24}$$

[$\phi_j(k)$ is some adequately chosen phase] and, subsequently, set up the secular equation in terms of the latter. In that event, the result is again the VPA relation Eq. (13). The other alternative is to determine the Wannier functions directly by expanding them in terms of the basis functions in the first line of Eq. (3),

$$w_{jp}(\vec{r}) = \sum_{mq} C^w_{m,p-q,j}\chi_{mq}(\vec{r}). \tag{25}$$

Here, we have used the fact that $w_{j,p+1}(\vec{r}) = w_{jp}(\vec{r}-\vec{a})$, which implies that the expansion coefficients depend only on $p-q$. The secular equation that one obtains is no longer an eigenvalue relation because the Lagrange multipliers for the orthonormality constraint do not satisfy $\lambda_{j_1j_2} = \epsilon_{j_1}\delta_{j_1,j_2}$. This poses a number of well-known disadvantages (see, for example, Ref. 41).

In summary, then, for electrostatic fields the scalar potential approach leads either to the same secular equation as the VPA or a secular equation that, on the face of it, appears more problematic to handle. For time-dependent fields, the VPA is the natural way to proceed since the formulation is the same as for static fields.

III. SOLVING THE VECTOR POTENTIAL APPROACH EQUATION

As we have argued above, the VPA secular equation for infinite periodic systems in external electrostatic fields leads to the most appealing formulation, i.e., Eq. (15), from a computational perspective. (An identical formulation may be developed from the MTP point of view since $P_{\mathrm{KSV}}=P_{\mathrm{VPA}}$.) For practical computational purposes, the key aspect involves smoothing and differentiating the coefficients $\{C_{qj}(k)\}$ with respect to k.

As seen in Eq. (23), $P_{\mathrm{KSV}}=P_{\mathrm{VPA}}$ can be split into two terms. The first of these, namely, P_1, can be evaluated through standard matrix multiplications involving known quantities. P_2 requires, in addition, derivatives of the orbital expansion coefficients with respect to k. It is most convenient to carry out the differentiation numerically as described in this section. In Ref. 32, an analytical alternative was presented. However, that treatment was developed specifically for use in conjunction with a perturbative solution of the secular equation, and is not appropriate as it stands for the finite field case. Furthermore, there are theoretical reasons (see below) to prefer the numerical procedure presented here.

Note that the calculated coefficients contain an arbitrary (random) k-dependent phase factor. The numerical differentiation will be problematic unless something is done to compensate for this randomness. Thus, an additional phase factor is introduced, i.e.,

$$C_{qj}(k) \to C_{qj}(k)e^{i\tilde{\phi}_j(k)}, \tag{26}$$

which is chosen so that the change in the coefficients from one k point to the next is minimized. After a very large number of exploratory studies, we have arrived at the following multistep procedure starting with the field-free expansion coefficients $\{C_{qj}(k)\}$ obtained by solving the single-particle equation:

(1) In real band-structure calculations, the orbitals are usually obtained in the order of increasing band energy for each k point separately. For numerical differentiation of the orbital expansion coefficients, it is important to join band orbitals at different k points correctly. Thus, we first identify band crossings. Assuming that orbitals for the same band have very similar expansion coefficients, we can identify band crossings from the relation

$$\sum_q C^*_{qj}(k)C_{qj}(k+\Delta k) \leqslant \delta_C, \tag{27}$$

for each band (j) and k value. (For $k=\frac{\pi}{a}$, $k+\Delta k$ is replaced by $-k+\Delta k$.) If the sum is smaller than the chosen threshold, δ_C, the orbitals are taken as belonging to two different, crossing bands and the coefficients $C_{qj}(k+\Delta k)$ and $C_{q,j+1}(k+\Delta k)$ are interchanged. A subsequent check is carried out to see whether Eq. (27) is still satisfied (i.e., whether more than two bands are crossing), in which case a further interchange of the orbitals at $k+\Delta k$ is carried out.

(2) When two or more band orbitals are energetically degenerate at a given k point, we construct linear combinations that are maximally similar to those of the two neighboring k points.

(3) After the resulting coefficients $\{C_{qj}(k)\}$ have been modified according to steps 1 and 2, we modify all coefficients at $k=0$ so that they are real.

(4) Starting from $k=0$ and $\tilde{\phi}_j(0)$, we consider consecutive positive k points and minimize

$$Q_j(k+\Delta k) = \sum_q |C_{qj}(k+\Delta k)e^{i\tilde{\phi}_j(k+\Delta k)} - C_{qj}(k)e^{i\tilde{\phi}_j(k)}|^2 \tag{28}$$

by varying $\tilde{\phi}_j(k+\Delta k)$. For negative k,

$$C_{qj}(-k)e^{i\tilde{\phi}_j(-k)} = C^*_{qj}(k)e^{-i\tilde{\phi}_j(k)}. \tag{29}$$

By deriving closed expressions for $\tilde{\phi}_j(k+\Delta k)$, this transformation is readily carried through. It leads to coefficients that are smooth as a function of k for $-\frac{\pi}{a}<k<\frac{\pi}{a}$, but discontinuities may occur at the zone boundaries.

(5) In order to remove discontinuities at $k=\pm\frac{\pi}{a}$, the quantity

$$Q_j = \sum_k \sum_q |C_{qj}(k+\Delta k)e^{i\tilde{\phi}_j(k+\Delta k)} - C_{qj}(k)e^{i\tilde{\phi}_j(k)}|^2 + \lambda \sum_k \sum_q |C_{qj}(k+2\Delta k)e^{i\tilde{\phi}_j(k+2\Delta k)} - C_{qj}(k)e^{i\tilde{\phi}_j(k)}|^2 \tag{30}$$

is minimized for each band j under the constraint

$$\tilde{\phi}_j\left(-\frac{\pi}{a}\right) = \tilde{\phi}_j\left(\frac{\pi}{a}\right), \tag{31}$$

and with $\tilde{\phi}_j(0)$ fixed. The first term in Eq. (30) makes the coefficients between neighboring k points maximally similar. However, it proved useful to include a next-nearest neighbor term as well. This improves the numerical stability of the derivatives with respect to k. Our studies showed that a reasonable value for λ is $\lambda=0.1$.

This is the time-consuming step in the overall smoothing procedure. It involves a nonlinear optimization that is carried out using conjugate gradients. The four preceding steps are necessary in order to provide a good initial guess. Experience has shown that for about 100 k points, on the order of a few hundred conjugate-gradient iterations are necessary. We emphasize that it is done only for zero field and, for a typical problem, will require just a small fraction of the overall computation time.

(6) By means of the above steps, we arrive at a set of smooth coefficients for the field-free case, $\{\tilde{C}_{qj}(k)\}$. These coefficients are used to evaluate the polarization for $E_{\mathrm{dc}}=0$ according to Eq. (23).

(7) For $E_{\mathrm{dc}}\neq 0$, we begin with steps 2 and 3 and, then, skip to step 8 below. It is thereby assumed that $E_{\mathrm{dc}}\neq 0$ does not remove band crossings by lowering the symmetry and that the field does not change the orbitals significantly. This was found to be the case in all our tests, and is preferable to repeating steps 4–7 as far as smoothing is concerned as well as for computational efficiency. However, it is also possible instead to repeat steps 4–7 as our model calculations confirmed.

(8) Subsequently, the coefficients are made maximally similar to those of the field-free case, i.e., for each band and k value we minimize,

$$\tilde{Q}_j(k) = \sum_q |C_{qj}(k) e^{i\tilde{\phi}_j(k)} - \tilde{C}_{qj}(k)|^2 \tag{32}$$

by varying $\tilde{\phi}_j(k)$. Compared to the case of $E_{\mathrm{dc}}=0$, where step 5 was time consuming, for the case of $E_{\mathrm{dc}} \neq 0$, steps 7 and 8 are computationally fast.

(9) Finally, all phases are modified by a k-independent but band-dependent constant so that the coefficients at $k=0$ are all real. This step is done only for aesthetic reasons!

Our smoothing approach leads ultimately to coefficients $\{C_{qj}(k)\}$ that are smooth functions of k. Therefore, numerically stable derivatives can be obtained from

$$\frac{\partial C_{qj}(k)}{\partial k} \simeq \frac{1}{\Delta k} \sum_{n=1}^{N_k} w_{n,N_k} [C_{qj}(k + n \cdot \Delta k) - C_{qj}(k - n \cdot \Delta k)] \tag{33}$$

with

$$C_{qj}\left(k + \frac{2\pi}{a}\right) = C_{qj}(k). \tag{34}$$

The most frequently used approximation is to take $N_k=1$. However, test calculations showed that an improved accuracy was obtained by using larger N_k. In that event, the coefficients $\{w_{n,N_k}\}$ are taken from Dvornikov.[40] Typically, $N_k \simeq 10$ leads to accurate results.

In an earlier work, Bishop *et al.*[32] wrote $\frac{\partial C_{qj}(k)}{\partial k}$ as $\Sigma_p C_{pi}(k) Q_{ij}(k)$ and gave an analytical prescription for determining $\underline{\underline{Q}}(k)$. This procedure relies on making a particular coefficient $C_{qj}(k)$ purely real for all k. However, that coefficient may vary considerably in importance as one goes across the first Brillouin zone, and it is not ensured that the discontinuity in the eigenvector is minimal when crossing the zone boundary. In our numerical studies, we found that the latter condition, embodied in step 5 above, is an important ingredient.

IV. MODEL CALCULATIONS

We have analyzed our approach using a modified Hückel-type model for the Hartree-Fock Hamiltonian in the VPA treatment of a 1D system [cf. Eq. (15)]. Similar considerations should apply to a Kohn-Sham Hamiltonian (see further discussion in Sec. V A). The modifications described below allow for the basis function flexibility and self-consistency that would be present in an *ab initio* calculation. At the same time, the simplicity of the model makes it possible to extensively explore convergence behavior, accuracy, and other issues of importance.

We emphasize that model calculations can never provide an ultimate test of our theoretical treatment. Care has been taken to introduce the most important features that would appear in an *ab initio* calculation, but other aspects, such as a more complicated band structure, could be of significance. On the other hand, we do wish to demonstrate that our treatment correctly reproduces results obtained for the corresponding finite system as the latter becomes very large. Even for our simple model, the field-dependent structure optimizations reported below for the finite system are computationally demanding and similar *ab initio* calculations with accurate electronic structure methods would be much more so.

A. Model

We consider linear A-B chains with alternating bond lengths. Nearest neighbor atoms are displaced by $\pm u_0$ from equidistant positions. Thus, for a lattice constant a, the alternating bond lengths are $\frac{a}{2} \pm 2u_0$. Our basis set consists of four orthonormal functions per atom, whose spatial parts are described through the two functions $\chi_{X,1}$ and $\chi_{X,2}$, with X being A or B. For each spatial orbital $\chi_{X,i}$, we consider the two spin orbitals $\chi_{X,i}\alpha$ and $\chi_{X,i}\beta$. Although the field-free Hamiltonian matrix elements are parametrized, simple analytical forms are introduced to obtain a consistent treatment of the two field-dependent terms in square brackets of Eq. (13). If z_0 is the position of atom X, we used $\chi_{X,1}(z) = \frac{1}{\sqrt{w_{X,1}}}$ for $|z - z_0| \leqslant \frac{w_{X,1}}{2}$, and zero elsewhere; $\chi_{X,2}(z) = \frac{1}{\sqrt{w_{X,2}}}$ for $\frac{w_{X,2}}{4} \leqslant |z - z_0| \leqslant \frac{w_{X,2}}{2}$, $\frac{-1}{\sqrt{w_{X,2}}}$ for $|z - z_0| \leqslant \frac{w_{X,2}}{4}$, and zero elsewhere. The widths w ($w_{X,1} > w_{X,2}$) were kept sufficiently small so that functions on non-neighboring atoms do not overlap.

Two-center matrix elements of the field-free Hamiltonian were assumed to vanish except for those between functions on neighboring atoms. Furthermore, the nonvanishing elements were taken to vary linearly as a function of interatomic distance. For each of the four nearest-neighbor basis function pairs, there are, accordingly, two parameters.

Self-consistency is introduced by treating the one- and two-electron contributions to the one-center matrix elements separately. The one-electron term $\langle \chi_{X,i}\sigma | \hat{h}_1 | \chi_{X,j}\sigma \rangle$ is taken to be nonzero only if $i=j$. For simplicity, the only two-electron terms retained are those where all four indices are the same, i.e., $\langle \chi_{X,i}\sigma_1 \chi_{X,i}\sigma_2 | v | \chi_{X,i}\sigma_1 \chi_{X,i}\sigma_2 \rangle$.

Once again, all field-free quantities are parametrized with values that depend on the particular basis function. Within this model, the Hartree-Fock-Roothaan equations for both infinite periodic chains and finite open chains contain all the complexities of an *ab initio* calculation. There are four basis functions per unit cell. In order to have a gap between the occupied and unoccupied molecular orbitals, each cell may have two, four, or six electrons. Positive charges are assigned to nuclei A and B to maintain cell neutrality.

All the ingredients for a VPA self-consistent field calculation of the electronic polarization, at fixed geometry, have now been given. For geometry optimization, we also include an elastic energy,

$$E_{\mathrm{elastic}} = \frac{f_1}{2} \sum_i \left(z_i - z_{i-1} - \frac{a_0}{2} \right)^2 + \frac{f_2}{2} \sum_i (z_i - z_{i-2} - a_0)^2, \tag{35}$$

where the summations run over all nearest and next-nearest neighbors of the system. By adjusting a_0, f_1, and f_2, it is

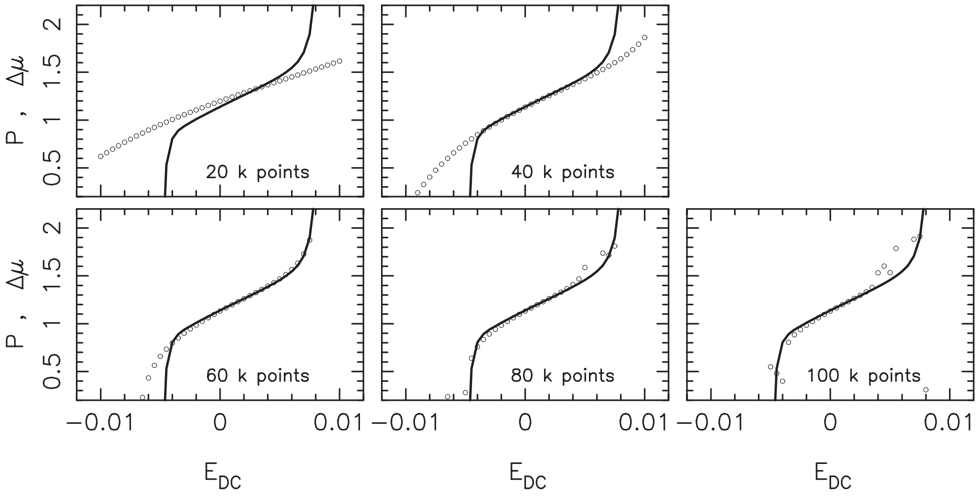

FIG. 1. Comparison of total polarization P for periodic chain (open circles) with corresponding finite-chain value (full curve), $\Delta\mu(K=25)$ [cf. Eq. (41)], as a function of field. All results were obtained at the same fixed geometry. The number of k points, K, used in the periodic chain calculations is given in the panels. Since P is defined only up to an additive integer multiple of the lattice constant, we have included such a term to make the periodic chain and finite-chain values agree as closely as possible. For further details, see the text.

possible to obtain any preselected lattice constant a and bond-length-alternation parameter u_0 for the field-free equilibrium geometry.

B. Behavior of self-consistent solutions as a function of K and E_{dc}

We now use the model of the preceding section to explore the behavior of the self-consistent VPA solutions for an infinite periodic chain exposed to a uniform static external electric field. As expected, this behavior depends on the number of k points as well as on the field strength. Figure 1 shows representative results for the total polarization

$$P = P_e + P_n, \tag{36}$$

with P_e being the self-consistent electronic polarization and P_n being the (classical) contribution for equal charges on the two nuclei. The results of Fig. 1 were calculated for the case of four electrons per unit cell. An additive integer multiple of the lattice constant has been included in P in order to make it agree as closely as possible with the comparison open chain value (see below). Note that the integer is not determined by the definition of P in Sec. II B.

With a few exceptions, to be discussed later, the SCF convergence criterion was set at 10^{-8}, i.e., we require that the Mulliken gross populations in the four atomic orbitals should differ, on average, by less than 10^{-8} from one iteration to the next. As a reference, the corresponding open chain values [cf. Eq. (41)], $\Delta\mu$ (K=25), are given by the solid curve in each panel. These values are not fully converged with respect to increasing chain length (see Sec. IV D), but they are sufficiently accurate for our purposes here. The steep turnover at either end of the solid curves is due to Zener tunneling (see below).

From Fig. 1, we see that about 40 k points, at least, are required to reproduce the reference open chain values in the region largely unaffected by Zener tunneling. Fortunately, using the VPA, SCF convergence is achieved at all fields in the region of interest for up to as many as 80 k points. Beyond that number, inaccurate outlying (off the curve) values begin to appear. These results are general; they do not depend critically on the parameters of the model. In addition, changing the number of k points used in the numerical differentiation [i.e., N_k of Eq. (33)] does not have an appreciable effect. As an aside, we note that for this particular choice of parameters and unit cell, the current term P_2 makes the dominant contribution to the electronic polarization at most fields.

There is a trade-off between SCF convergence and accuracy. The outlying values in Fig. 1 were found for the above convergence criterion. With a tighter requirement, the calculations did not diverge but, instead, became oscillatory. In general, a looser requirement for convergence implies a less accurate value for P_e. It is important, therefore, to make the tolerance as tight as possible without inducing oscillatory behavior.

C. Band structure and threshold for Zener tunneling

Let us turn now to the band structure. According to Ref. 23, there is a simple relation between the zero-field highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) band gap, E_{gap}, and the approximate threshold dc field for field-induced electron tunneling (i.e., Zener tunneling) between the HOMO and LUMO bands:

$$E_{\mathrm{dc},t} = \frac{E_{\mathrm{gap}}}{Ka}. \tag{37}$$

The zero-field band structure possesses an avoided crossing of the HOMO and LUMO bands near $k=\pm\frac{\pi}{a}$, resulting in E_{gap}=0.2161 a.u. Using a=2.2 a.u., the predicted threshold field is $E_{\mathrm{dc},t}$=0.0012 a.u., which is well below the value

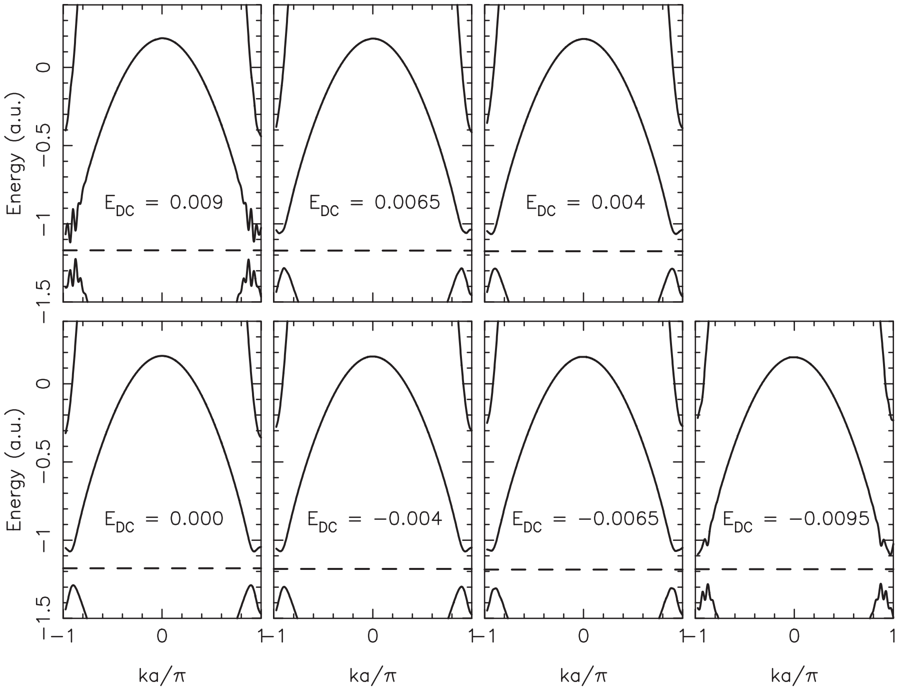

FIG. 2. Field-dependent band structures in the vicinity of the Fermi level ($K=80$).

where SCF convergence difficulties begin to occur in the VPA calculations. Approaches based on the MTP have also found that calculations could be carried out beyond the theoretical limit predicted by Eq. (37).[24,30] In addition, this result is consistent with the VPA field-dependent band structure (cf. Fig. 2) which is altered very little as E_{dc} is increased until the region of steep rise or fall in Fig. 1.

The onset of Zener tunneling effects in the VPA treatment is accompanied by characteristic wiggles near the HOMO and LUMO band edges. These wiggles are associated with the phase factor of the orbitals. The connection between the two may be understood by reference to Eq. (13). From the latter, one can see that multiplication of the coefficients by a phase factor

$$\underset{\sim}{C}_j(k) \rightarrow e^{i\theta_j(k)} \cdot \underset{\sim}{C}_j(k) \tag{38}$$

will give rise to an augmented field-dependent orbital energy:

$$\epsilon_j(k) \rightarrow E_{\mathrm{dc}} \frac{d}{dk} \theta_j(k) + \epsilon_j(k). \tag{39}$$

In this connection, note that the smoothing procedure described in Sec. III is not unique. Any additional phase factor that maintains smoothness (while satisfying the boundary condition) is acceptable and may be included in $\theta_j(k)$. The consequences of such nonuniqueness, as far as the band structure is concerned, deserves further study. For this paper, however, we have considered alternative smoothing procedures only with regard to obtaining SCF convergence for maximally large fields. Zener tunneling will, in addition, affect the density of states and the ionization spectrum, which are also beyond the scope of the current paper.

D. Calculation of (hyper)polarizabilities

A sensitive test for the accuracy of P is afforded by the coefficients of the power series expansion,

$$P(E_{\mathrm{dc}}) = \mu_0 + \alpha_0 \cdot E_{\mathrm{dc}} + \beta_0 \cdot E_{\mathrm{dc}}^2 + \gamma_0 \cdot E_{\mathrm{dc}}^3 + \cdots , \tag{40}$$

which gives the (non)linear unit cell susceptibilities in the zero-field limit. (This differs from the more common Taylor series expansion by factors of $n!$, which make no difference for our analysis.) Again, it is useful to compare with open chain reference calculations where P is replaced by

$$\Delta\mu(K) = \mu(K+1) - \mu(K), \tag{41}$$

and the same model, parameters, and SCF convergence criterion are employed. The expansion coefficients for open chains (shown in the right-hand panels of Fig. 3) were determined from a least squares fit of a third-order polynomial to results (where available) for a set of fields $\{E_{\mathrm{dc}}\}$ up to a maximum $|E_{\mathrm{dc}}| = E_{\mathrm{dc,max}}$. We considered the following 73 values for E_{dc}: 0.000, $\pm n \cdot 0.001$, $n=1,2,\ldots,20$, and $\pm n \cdot 0.005$, $n=5,6,\ldots,20$. Fits to forth- and fifth-order polynomials were carried out as well with no differences observed except for larger values of $E_{\mathrm{dc,max}}$. As usual, fewer calculations converge as the magnitude of the field and the chain length is increased. The $K=25$ values were used as a reference in Fig. 1. Although accurate enough for our previous purposes, Fig. 3 shows they are not sufficiently converged with respect to system size to give a satisfactory β_0 or γ_0. In fact, it is difficult, or impossible, to obtain a converged finite-chain value of γ_0 for the case at hand. Instead, K above 50 should be used for the finite-chain calculations. For the periodic chain calculations, as many as 80–100 k points are necessary to achieve convergence.

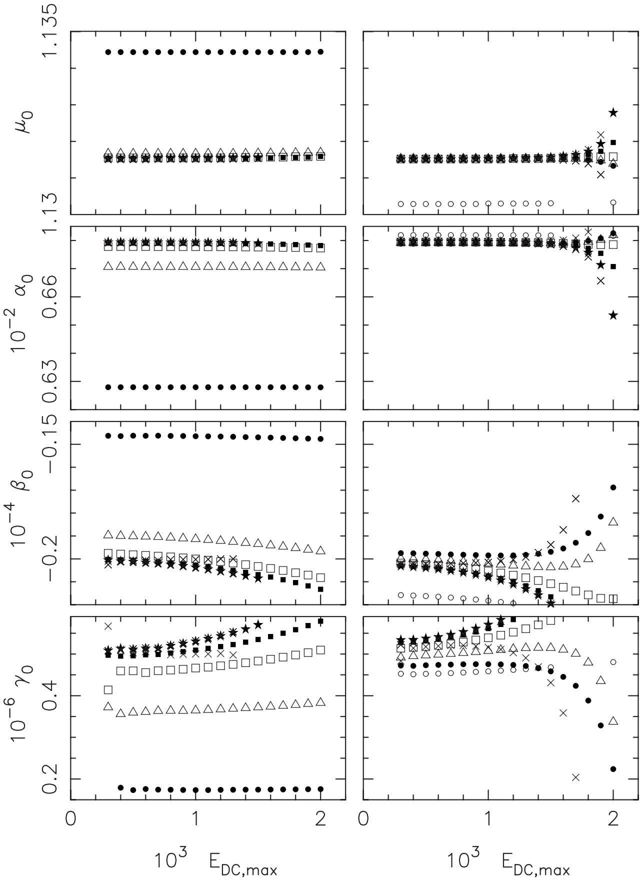

FIG. 3. The expansion coefficients μ_0, α_0, β_0, and γ_0 of Eq. (41) for the dipole moment increment (right column) of finite chains and the polarization of periodic chains (left column) as a function of the maximum field included in the fitting. Finite chains with 29 as well as 50, 51, …, 55 units were considered. In the left column, open circles, filled circles, open triangles, open squares, filled squares, stars, and crosses mark values for K=20, 40, 60, 80, 100, 150, and 200, respectively, whereas the same symbols in the right column are used for K=29, 50, 51, 52, 53, 54, and 55, respectively.

It is satisfying that, in the zero-field limit, the converged periodic chain coefficients agree very closely with those obtained for the longest open chains and show a much better defined approach to the limit value. As a general procedure, the most accurate results may be found by considering a few fields of low absolute magnitude. We note that the open chain coefficients are subject to much more scatter than those obtained for the periodic chain. As expected, γ_0 is the parameter that shows the largest scatter.

V. CALCULATION OF STRUCTURAL RESPONSES

So far we have dealt entirely with the pure electronic polarization response to E_{dc}. The field will also alter the potential energy surface and thereby induce a nuclear response. In this section, our focus will be on the change in equilibrium geometry, i.e., the nuclear relaxation, although all phonon properties will be affected. In order to determine the nuclear relaxation, we need to calculate field-dependent forces. It is most efficient to do such calculations analytically rather than numerically. To that end, we derive an analytic formula for the VPA forces induced in an infinite periodic system by an external uniform dc field. Subsequently, this formula will be applied to determine the field-dependent nuclear relaxation of our model system and compared with results for finite open chains.

A. Analytical forces

For the purposes of this paper, we consider specifically the Hartree-Fock (HF) approximation, which is consistent with the model of Sec. III. It is convenient to follow the derivation used by Zerner.[43] However, any existing formulation for field-free molecules could be employed, together with suitable modifications for the polarization term and the periodicity, as done here. An alternative to our treatment has been presented by Jacquemin *et al.*[44] The same considerations apply to Kohn-Sham DFT, although there is no suitable functional at present with which to treat the polarization of long chains.[45,46]

For an infinite periodic chain in a dc field, the HF approximation is given by Eq. (13), while the corresponding energy formula for one BvK zone of K units is

$$E_e = E_e^0 - E_{\mathrm{dc}}\sum_k\sum_j\sum_{pq}\Bigg[iC^*_{qj}(k)\frac{\partial C_{pj}(k)}{\partial k}S_{qp}(k) + C^*_{qj}(k)C_{pj}(k)M_{qp}(k)\Bigg]. \tag{42}$$

In Eq. (42),

$$E_e^0 = \sum_k\sum_{pq}P_{qp}(k)h_{qp}(k) + \frac{1}{2}\sum_{k_1k_2}\sum_{p_1p_2q_1q_2}P_{q_1p_1}(k_1)P_{q_2p_2}(k_2)v_{q_1q_2p_1p_2}(k_1,k_2) \tag{43}$$

is the expression whose derivative was studied by Zerner (although here, of course, the density matrix $\underline{\underline{P}}$ is a function of the field). Taking the new E_{dc} terms into account, we arrive, after some manipulation, at the intermediate result

$$\frac{\partial E_e}{\partial x} = \sum_k\sum_{pq}P_{qp}(k)\frac{\partial h_{qp}(k)}{\partial x} + \frac{1}{2}\sum_{k_1k_2}\sum_{p_1p_2q_1q_2}P_{q_1p_1}(k_1)P_{q_2p_2}(k_2)\frac{\partial v_{q_1q_2p_1p_2}(k_1,k_2)}{\partial x} - \sum_k Q_{pq}(k)\frac{\partial S_{qp}(k)}{\partial x} - iE_{\mathrm{dc}}\sum_k\sum_{pq}R_{qp}(k)\frac{\partial S_{qp}(k)}{\partial x} - E_{\mathrm{dc}}\sum_k\sum_{pq}P_{qp}(k)\frac{\partial M_{qp}(k)}{\partial x} - E_{\mathrm{dc}}\sum_j\sum_k\sum_{pq}\Bigg[iS_{qp}(k) \times\left(C^*_{qj}(k)\frac{\partial}{\partial k}\frac{\partial C_{pj}(k)}{\partial x} + \frac{\partial C^*_{qj}(k)}{\partial k}\frac{\partial C_{pj}(k)}{\partial x}\right)$$

$$+ C^*_{qj}(k)\frac{\partial C_{pj}(k)}{\partial x}[M_{qp}(k) - M^*_{pq}(k)]\Bigg], \tag{44}$$

in which

$$R_{qp}(k) = \sum_j C^*_{qj}(k)\frac{\partial C_{pj}(k)}{\partial k},$$

$$Q_{qp}(k) = \sum_j \epsilon_j(k) C^*_{qj}(k) C_{pj}(k), \tag{45}$$

and x is a parameter in the electronic Hamiltonian, taken here to be a structural parameter.

In order to proceed further, we note that the electronic polarization must be real, i.e., $P_e = P_e^*$, and therefore

$$\sum_k \sum_j \sum_{pq}\Bigg[-iC^*_{qj}(k)\frac{\partial C_{pj}(k)}{\partial k}S_{qp}(k) - i\frac{\partial C^*_{qj}(k)}{\partial k}C_{pj}(k)S_{qp}(k) + C^*_{qj}(k)C_{pj}(k)[M^*_{pq}(k) - M_{qp}(k)]\Bigg] = 0. \tag{46}$$

Using the definitions of Eq. (8), this means that

$$\frac{\partial S_{qp}(k)}{\partial k} = -i[M_{qp}(k) - M^*_{pq}(k)]. \tag{47}$$

Then, we take the x derivative of Eqs. (46) and (47), and utilize the fact that

$$\sum_k \frac{\partial f}{\partial k} = 0, \tag{48}$$

for any f of interest, since

$$f\left(k = \frac{\pi}{a}\right) = f\left(k = -\frac{\pi}{a}\right). \tag{49}$$

This leads to our final expression,

$$\frac{\partial E_e}{\partial x} = \sum_k \sum_{pq} P_{qp}(k)\frac{\partial h_{qp}(k)}{\partial x} + \frac{1}{2}\sum_{k_1k_2}\sum_{p_1p_2q_1q_2} P_{q_1p_1}(k_1)P_{q_2p_2}(k_2)\frac{\partial v_{q_1q_2p_1p_2}(k_1,k_2)}{\partial x} - \sum_k Q_{pq}(k)\frac{\partial S_{qp}(k)}{\partial x} - \frac{E_{\mathrm{dc}}}{2}i\sum_k\sum_{pq}[R_{qp}(k) - R^*_{pq}(k)]\frac{\partial S_{qp}(k)}{\partial x} - \frac{E_{\mathrm{dc}}}{2}\sum_k\sum_{pq}P_{qp}(k)\left(\frac{\partial M_{qp}(k)}{\partial x} + \frac{\partial M^*_{pq}(k)}{\partial x}\right), \tag{50}$$

which we have also verified numerically.

B. Results

As discussed in Sec. IV A, the structure of the infinite periodic chain can be described by the lattice constant, a, and the bond-length-alternation (BLA) parameter, $\pm u_0$, which gives the alternating bond lengths $\frac{a}{2}\pm 2u_0$. On the other hand, for the reference finite chain of K units, the $2K-1$ interatomic distances may all be different. In that event we, first, place the chain along the z axis so that $\Sigma_n z_n = 0$ (z_n is the z coordinate of the nth atom, $n = 1, 2, \ldots, 2K$) and, then, define the quantity $u_n = z_n - \left(n - K - \frac{1}{2}\right)\frac{a}{2}$ (here, a is the lattice constant for the periodic system) as the site-dependent replacement for $\pm u_0$. In Fig. 4, the left-hand panels show the zero-field values of u_n for finite chains of 27 and 52 units. Although the zero-field curves are similar for the two chains, the field-induced nuclear relaxation is quite different as seen in the right-hand panels of Fig. 4. Only small fields are included because the structural changes induced by larger fields do not fit on the plot. For the shorter chain on the right, it is difficult to identify a central region where the curves are nearly flat. Even for the longer chain, the field-induced structural changes are not perfectly behaved in the central region.

In order to estimate a and u_0, we consider the lengths of the middle bond, d_2, as well as the two neighboring bonds, d_1 and d_3. From the average of the latter, $d_{13} = \frac{d_1 + d_3}{2}$, we estimate $a = d_2 + d_{13}$ and $u_0 = \frac{\pm 1}{4}(d_2 - d_{13})$, where $+(-)$ is used if K is odd (even). These results are compared with the structure of the infinite periodic chain in Fig. 5. Clearly, the finite chain with 27 units is too short to provide an accurate estimate for the field-dependent geometry of the infinite periodic chain. On the other hand, the finite chain with 52 units and the periodic chain are in excellent agreement (even though the former is not fully converged with respect to chain length). Although it is possible that jumps in P_e (by an integral multiple of the lattice constant) could have occurred during the course of our geometry optimizations, there is no evidence to that effect. Note also that, for the model parameters used here, a depends only weakly on the field as compared to u_0.

In Fig. 6, we show the polarization as a function of field strength, i.e., the analog of Fig. 1 with nuclear relaxation now included. The agreement between the finite chain and periodic chain results is excellent. As before, these results can be expanded as a power series in the field. Now the coefficients include an approximate correction for vibration, in addition to the pure electronic property, all evaluated at the field-free geometry.[47] The coefficient values are more affected by numerical inaccuracy than those given for fixed geometry. Converged values of β_0 and γ_0 for the finite chains and γ_0 for the infinite chains are poorly determined. This is not too surprising because of the additional opportunity for inaccuracy associated with the geometry optimization. Nevertheless, it is interesting that the nonlinear expansion coefficients are strongly affected by nuclear relaxation. Whereas the linear coefficient changes by about +3%, the quadratic and cubic coefficients change by −30% and +220%, respectively. This is consistent with the large effects found in many molecular *ab initio* calculations.[48]

VI. SOME IMPLICATIONS FOR FINITE PUSH-PULL CHAINS

Let us consider a neutral system containing K repeated units terminated by, say, an electron donor group on one end and an electron acceptor group on the other (a so-called

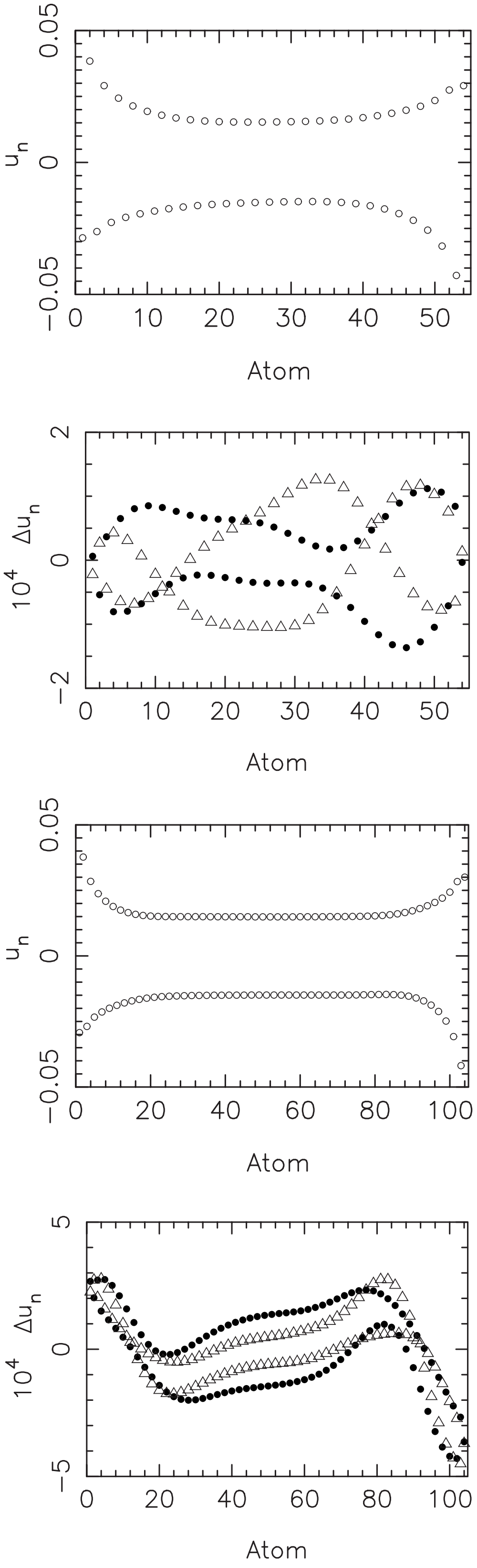

FIG. 4. Field-induced nuclear relaxation for finite open chains with 27 units (upper panels) and 52 units (lower panels). The panels show the reference zero field u_n (see text for definition) and the changes Δu_n due to the presence of the field. Open circles, filled circles, and open triangles mark results for field strengths of 0.000, 0.001, and −0.001 a.u., respectively.

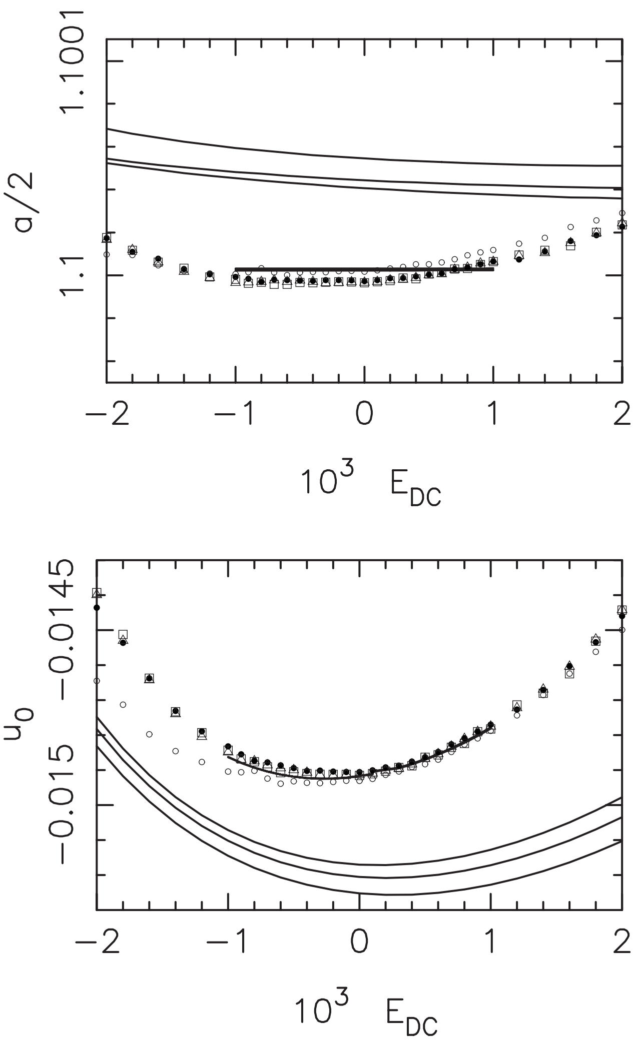

FIG. 5. Optimized values of $\frac{a}{2}$ (upper panel) and u_0 (lower panel) as a function of the field. The solid curves (from top to bottom on the upper panel, and from bottom to top on the lower panel) are for finite chains with K=25, 26, 27, 50, 51, and 52 units (not all the curves are resolved). Open circles, filled circles, open triangles, and open squares are for periodic chains calculated using 40, 60, 80, and 100 k points, respectively.

push-pull system). As usual, we need to specify the repeat unit (with or without substituents) precisely in order to have a well-defined polarization. [The polarization of an (A-B)…(A-B) chain, for example, differs from that of a (B-A)…(B-A) chain.] Then, if the chain is sufficiently long, it may be divided into a central region and two terminal regions. The former is assumed to consist of identical neutral units that are essentially unaffected by the chain termination. Although the exact boundary between the regions is to some extent arbitrary, additional unit cells are clearly assignable to the central region, while leaving the terminal regions unaltered in length, as shown in Ref. 42 for a more problematic (i.e., more delocalized) case. As long as the above conditions are met, we will see that the terminal groups are arbitrary.

Assuming that the chain is lying along the z axis and considering only the z component of the dipole moment, we

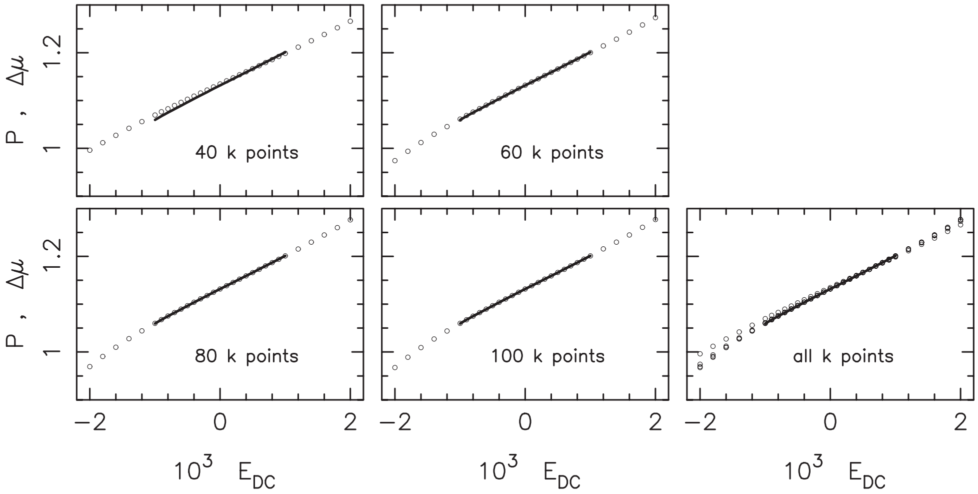

FIG. 6. Same as in Fig. 1, but with nuclear relaxation included. In this case, the full curve marks results for finite chains with $K=51$ units.

define the polarization (i.e., the dipole moment per unit cell) as

$$P = \lim_{K\to\infty}[\mu(K)/K] = \lim_{K\to\infty}[\mu(K) - \mu(K-1)]. \qquad (51)$$

If $\rho(\vec{r})$ is the total charge density (i.e., the sum of the nuclear and electronic charge densities), then the total dipole moment is

$$\mu = \int \rho(\vec{r})z d\vec{r} = \int_L \rho(\vec{r})z d\vec{r} + \int_C \rho(\vec{r})z d\vec{r} + \int_R \rho(\vec{r})z d\vec{r}, \qquad (52)$$

where we have split the integral into contributions from the left (L), central (C), and right (R) regions of the chain. Since the central region consists of identical neutral units, we can write

$$\int_C \rho(\vec{r})z d\vec{r} = K_C \mu_C, \qquad (53)$$

where K_C is the number of units in C and μ_C is the dipole moment of one of these units. In order to evaluate the other two contributions to the total dipole moment in Eq. (52), we define for each a "typical" center, $\vec{R}_R$ and $\vec{R}_L$ (these could, e.g., be the center of mass of the right and left parts, respectively), and let Z_R and Z_L be the z components of these vectors. Since the total chain is neutral we, then, obtain

$$\int_L \rho(\vec{r})z d\vec{r} + \int_R \rho(\vec{r})z d\vec{r} = (Z_R - Z_L)\int_R \rho(\vec{r})d\vec{r} + \int_L \rho(\vec{r})(z - Z_L)d\vec{r} + \int_R \rho(\vec{r})(z - Z_R)d\vec{r}. \qquad (54)$$

Here, the first term describes the contribution to the dipole moment associated with electron transfer from one end to the other. This term grows linearly with chain length (due to $Z_R - Z_L$) as is the case for the term in Eq. (53). On the other hand, the last two terms in Eq. (54) describe local dipole moments that arise from the electron distributions within the two terminal regions and are independent of the chain length.

The above analysis shows immediately that the polarization has one contribution from the central region and another from the terminal regions. This is consistent with the description of the polarization as a bulk property,[16,49] developed from the Wannier function point of view [cf. Eq. (21)]. It follows that P must be independent of the terminal groups (at least, when assuming that the chain ends are taken to be long enough so that they do not influence the charge distribution and structure in the central region). Accordingly, for a sufficiently long finite chain, the charge transfer from one end to the other

$$q = \int_R \rho(\vec{r})d\vec{r} \qquad (55)$$

will always be the same (in our earlier work,[9] we gave a numerical example of this finding) regardless of how the chain is terminated. Even for a very long chain, there remains a *possibility* that an integral number of electrons will be transferred depending on the chemical nature of the end groups. Hence, we must add the additional proviso that this does not occur.

If the repeated unit is centrosymmetric, then the value of q can be determined by considering the special case where the two ends are identical. In that event, the total system is also centrosymmetric and q must be zero. Thus, with the assumptions already discussed, there will be no net flow of charge from one end to the other, no matter what kind of substitution is introduced at the ends.

In the presence of a finite field, all of the above analysis remains valid except that the charge transfer is nonzero even for a centrosymmetric repeat unit. This is true whether or not one allows for nuclear relaxation. The static (hyper)polarizabilities will, then, be independent of the end groups, again with the same provisos as before (for an example, see Ref. 50).

VII. SUMMARY AND OUTLOOK

We have presented in detail the vector potential approach (VPA) for calculating the Bloch orbitals, and the electronic polarization (P_e), of an infinite periodic polymer subjected to a uniform finite (static) electric field. In this case, the VPA equation for the band energies and crystal orbitals can be converted into a standard matrix eigenvalue problem, which must be solved self-consistently. It is also possible to put the scalar potential approach in the same computationally advantageous form, as we have shown, although current MTP treatments do not do so. The occupied orbital eigenvectors that emerge from matrix diagonalization must be smoothed as a function of k in order to obtain accurate derivatives needed for evaluating the contribution of P_e to the effective Hamiltonian. This is done by introducing k-dependent phase factors that minimize the change in the eigenvectors from one k point to the next. An efficient multistep procedure that yields the desired smoothing is described.

In order to investigate the key features of our SCF treatment, extensive calculations were carried out for an A-B linear chain using a Hückel-type model. This model was carefully constructed to be internally consistent and to include the major complexities of an *ab initio* Hartree-Fock (or Kohn-Sham) calculation. On the other hand, due to its simplicity, finite system calculations could be carried through for systems that were so large that finite size effects could be eliminated, thereby leading to the ultimate validation of our approach for infinite, periodic systems.

For infinite periodic chains, there is good SCF convergence even when a large number of k points is needed for accurate results (due to strong delocalization). Furthermore, SCF convergence can be obtained at fields well beyond the usual threshold estimate for Zener tunneling. Eventually, tunneling does lead to convergence failure and/or inaccuracies. At the same time, wiggles appear near the edges of the highest occupied and lowest unoccupied field-dependent bands. Both of these effects are associated with wiggles in the orbital phase factors. For optimum results, one wants to make the convergence criterion as tight as possible without inducing oscillations.

In addition to inducing electronic polarization, a finite field will modify the potential energy surface and, consequently, alter the equilibrium geometry. The resulting nuclear relaxation is most efficiently calculated using analytical forces. We have derived an expression for the forces using the Hartree-Fock VPA equation and applied it to obtain the field-dependent unit cell length and BLA parameter of our model system. A power series fit of the polarization, as a function of field, yields large changes in the nonlinear coefficients due to nuclear relaxation.

The fact that polarization is a bulk property has implications for long finite chains. In particular, we show (with certain limited assumptions) that terminal substitutions on a chain of repeated units cannot affect the field-dependent polarization. This is true regardless of the nature of the substituents and whether or not nuclear relaxation is taken into account.

Although our presentation has been restricted to the case of quasi-1D systems, it should be possible to extend the basic treatment to more dimensions. Formally, one simply replaces the scalar k with vector $\vec{k}$, and the 1D lattice vector $\vec{a}$ with the 2D or 3D vector $\vec{R}$. Since the band structure can be more complex than we have considered here, details may change, particularly with regard to the optimum smoothing procedure. This is a subject for future study. In addition, we plan to examine further polymer applications and to add magnetic fields. The VPA would seem to be especially appropriate for properties that depend simultaneously on magnetic and electrical fields.

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