

Berry phase approach to longitudinal dipole moments of infinite chains in electronic-structure methods with local basis sets

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The authors provide a reformulation of the modern theory of polarization for one-dimensional stereoregular polymers, at the level of the single determinant Hartree-Fock and Kohn-Sham methods within a basis set of local orbitals. By starting with localization of one-electron orbitals, their approach naturally arrives to the Berry phases of Bloch orbitals. Then they describe a novel numerical algorithm for evaluation of longitudinal dipole moments, computationally more convenient than those presently implemented within the local basis periodic codes. This method is based on the straightforward evaluation of the usual direct space dipole matrix elements between local orbitals, as well as overlap matrices between wave functions at two neighboring k points of the reciprocal space mesh. The practical behavior of the algorithm and its convergence properties with respect to the k -point mesh density are illustrated in benchmark calculations for water chains and fluorinated *trans*-polyacetylene. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743018]

I. INTRODUCTION

The dipole moment of a *finite* oligomer is a simple quantity. In fact, its electronic contribution is the first moment of the density, which is obviously well defined for any bound state, where the density vanishes exponentially at infinity. An alternative definition of the dipole is via the first derivative of the energy with respect to the external electric field: this is the only possible choice in some correlated *ab initio* methods with unnormalized wave functions such as the coupled-cluster method. For long polymeric chains the longitudinal dipole d is an extensive quantity (proportional to the length); hence it is more appropriate to address the dipole p per monomer (i.e., per unit cell). We draw attention to a semantic issue: despite using the symbol p , we carefully avoid throughout this work using the word “polarization,” which—in our view—has been misused in some of the quantum-chemistry literature and could therefore generate confusion.

When studying stereoregular quasi-one-dimensional (quasi-1D) polymers at either the Hartree-Fock (HF) or density-functional level, it is quite convenient to exploit translational symmetry by addressing infinite chains, where the HF canonical orbitals, as well as the Kohn-Sham (KS) orbitals, assume the Bloch form. The first moment of the density, however, becomes ill defined. Thus the dipole needs quite a different treatment than in finite systems. Problems also appear while trying to define the moment as the first order response to the electric field operator $\langle \mathbf{r} \rangle$, since such an operator breaks the translational periodicity of the system. A

well-known fix is to switch to the vector-potential gauge where, however, then the Hamiltonian becomes a time-dependent one.

Methods for dealing with the changes in dipole (such as infrared charge tensors and polarizability) *induced* by a given noncentrosymmetric perturbation in an infinite chain have been known for a long time. Within the quantum-chemistry literature it is customary to quote a paper by Genkin and Mednis,¹ while the analogous method in solid-state physics is attributed to earlier papers by Adler and Wiser.² Over the years other more efficient methods for evaluating induced dipoles have been developed.³ In addition, higher order derivatives such as hyperpolarizabilities have been successfully addressed as well.^{4,5}

At variance with this, the problem of evaluating the “dipole itself” (for example, defined as an infinite limit of the dipole moment per unit in oligomers of increasing size) remained an open and confusing one until the mid-1990s when the advent of the modern theory of polarization, based on a Berry phase, provided a resolution.^{6–10} Among other things, the modern theory opened new avenues for first-principles studies of ferroelectric materials.^{11,12} Nowadays, the Berry phase expressions for the dipole are implemented as a standard option in most electronic-structure codes for crystalline solids.^{13–17}

Notwithstanding, in the quantum-chemistry literature the analogous problem of evaluating p in infinite linear chains has been until recently a confusing one and an area of ongoing research.^{18–21} While the properties derived from the intraband matrix elements (polarizability and higher) have been in use for quite some time,^{1,22,23} an expression for di-

pole moment has emerged only recently. Specifically, Bishop *et al.*²⁴ presented an approach which, while ultimately yielding the correct answer, requires one to make the complex orbital phases continuous in the reciprocal space and has not yet been implemented within the codes in the public domain. Later Jacquemin *et al.*²⁵ differentiated this expression in order to obtain first derivatives of the dipole with respect to the atomic displacements: these are the infrared charge tensors (also known as Born charges or dynamical charges in the condensed-matter literature). Very recently, a finite-field generalization of Ref. 24 has been published.²⁶

In this work we provide a reformulation of the modern theory of polarization, as applied to quasi-1D stereoregular polymers, described at either the HF or KS level. Compared to the earlier derivation of such expressions in the quantum-chemistry literature,²⁴ our formulation is given here in an alternative, and we believe more transparent way. It is based on the three important ingredients: localized orbitals (Boys type and Wannier), partitioning of the electronic charge distributions into localized charges, and finally, mapping the quantum-mechanical system into an equivalent system of point charges. This is quite novel in the quantum-chemistry literature and makes the comparison between finite and infinite chains quite natural. Also, with such an approach, the concept of the Berry phase gets introduced in a very pedagogical way, as the means to compute positions of the localized orbitals in periodic systems.

We also provide a novel numerical algorithm for evaluation of the longitudinal dipole moment within a basis set of local orbitals, more elegant and transparent than the approach by Bishop *et al.*,²⁴ and computationally more convenient than the Berry phase algorithms presently implemented within local basis codes, such as CRYSTAL (Ref. 14) and SIESTA.¹⁵ Our algorithm is in a sense “native” for local basis sets: it only requires the usual dipole and overlap matrix elements, while the one implemented in CRYSTAL (Ref. 27) requires instead the evaluation of plane-wave matrix elements over the basis.

We stress that in the present formulation we limit ourselves to the cases where either the Fock operator or the KS potential possesses the translational symmetry along the chain; hence, external electric fields are ruled out. The generalization of the modern theory of polarization to cases where a nonzero electric field is present does exist,^{28,29} but will not be considered here. Finally, the extension of our approach to the two-dimensional (2D) and three-dimensional (3D) periodic systems is rather straightforward, and for clarity of presentation is mentioned only briefly.

II. GENERALITIES

Let us consider a finite quasi-1D oligomer, with nuclei of charges Z_s at positions $\mathbf{r}_s = (x_s, y_s, z_s)$; let N_σ ($\sigma = \alpha, \beta$) be the number of electrons in each spin channel, i.e., the number of occupied spin-orbitals of a given spin. The z (i.e., longitudinal) component of the total dipole is

$$d = \sum_s Z_s z_s - \sum_\sigma \sum_{j=1}^{N_\sigma} \int d\mathbf{r} z |w_{\sigma j}(\mathbf{r})|^2, \quad (1)$$

where the w 's are single-particle spin-orbitals. Since Eq. (1) is invariant with respect to a unitary transformation of the occupied orbitals among themselves, we assume the w 's to be localized spin-orbitals, for instance, according to Boys's criterion.³⁰ This allows us to define the (z -projected) center of their electron distribution as

$$\bar{z}_{\sigma j} = \int d\mathbf{r} z |w_{\sigma j}(\mathbf{r})|^2, \quad (2)$$

and the dipole becomes

$$d = \sum_s Z_s z_s - \sum_\sigma \sum_{j=1}^{N_\sigma} \bar{z}_{\sigma j}. \quad (3)$$

We have therefore mapped our finite quantum-mechanical system onto an equivalent system of integer point charges. Notice that each of the two terms in Eq. (3) depends on the origin choice, while their sum provides an origin-independent, unambiguous dipole value. Overall, the charge neutrality of the system is essential in this respect.

If the quasi-1D system is stereoregular, we may also consider its infinite-length limit, which is periodical with period a in the z direction. The spin-orbitals (either HF or KS) $\varphi_{\sigma nk}$ are labeled by a band index n ($n \leq N_\sigma$) and by a 1D Bloch vector k . The Bloch theorem yields

$$\varphi_{\sigma nk}(\mathbf{r}) = e^{ikz} u_{\sigma nk}(\mathbf{r}), \quad (4)$$

and $u_{\sigma nk}(\mathbf{r})$ is lattice periodical:

$$u_{\sigma nk}(\mathbf{r}) = u_{\sigma nk}(\mathbf{r} + \mathbf{R}_l), \quad (5)$$

where $\mathbf{R}_l = (0, 0, la)$. We normalize the orbitals $\varphi_{\sigma nk}(\mathbf{r})$ to 1 over the period a (i.e., over one unit cell).

For an *insulating* infinite chain the localization transformation leads to Wannier orbitals^{31,32} of index n in cell l ,

$$w_{\sigma nl}(\mathbf{r}) = \frac{a}{2\pi} \int_0^{2\pi/a} dk e^{ikla} \varphi_{\sigma nk}(\mathbf{r}). \quad (6)$$

A well-known identity^{33,34} relates the z -projected center of the Wannier orbitals to the Berry phase as

$$\bar{z}_{\sigma nl} = \int d\mathbf{r} z |w_{\sigma nl}(\mathbf{r})|^2 = \frac{a}{2\pi} \gamma_{\sigma n} + la, \quad (7)$$

where the Berry phase of a band³³ is the real dimensionless number defined as

$$\gamma_{\sigma n} = i \int_0^{2\pi/a} dk \langle u_{\sigma nk} | u'_{\sigma nk} \rangle, \quad (8)$$

where $u_{\sigma nk}$ is the lattice periodical part of the Bloch orbital from Eq. (4), and the prime denotes the k derivative.

What is notable about Eq. (7) is that it allows one to map continuous bands to *integer* point charges located at

$$\bar{z}_{\sigma nl} = \frac{a}{2\pi} \gamma_{\sigma n} + la. \quad (9)$$

Then one can formally define the dipole value for a periodic point-charge system that includes nuclei and localized electrons as

$$p_0 = \sum_s Z_s z_s - \sum_{\sigma} \sum_{n=1}^{N_{\sigma}} \bar{z}_{\sigma nl}. \quad (10)$$

This periodic point-charge model system already has some interesting quantization properties. Specifically, if one were to shift the origin for any of the integer point charges (either nuclei or localized electrons) from z_i to an equivalent lattice point $z_i + ma$, the value of p_0 will change by an integer times a to p , and, in fact, such changes is the only possible outcome of any origin shift in a periodic system of integer point charges.

III. BERRY PHASE FORMULATION

The quantization of the allowed periodic dipole moment values found in a system of integer point charges naturally corresponds to a similar effect in quantum-mechanical systems even without any actual localization. There, it manifests itself as a topological property related to the occurrence of (Berry) phases,³⁵ which are defined modulo 2π . In our derivation earlier, the Berry phase appeared naturally as the way to compute positions of the Wannier orbitals in Eq. (7). Yet the transformation to Wannier orbitals is not really necessary, since one can compute the Berry phase directly for the conventional Bloch bands. Notably, the Berry phase approach leads to a very convenient computational algorithm to evaluate the nonquantized term p_0 in the dipole per cell p . The dipole per cell p , as discussed above, is equal to p_0 plus an integer times a .

For the sake of simplicity, we proceed from now on by assuming a *spin-unpolarized* ground state, where there are \bar{N} doubly occupied bands. The modifications needed for generalizing to the spin-polarized case (either unrestricted HF or local-spin density) are trivial enough to derive and will not be treated explicitly here. The electronic term in the periodic dipole, Eq. (10), is then

$$2 \sum_{n=1}^{\bar{N}} \bar{z}_{n0} = 2 \sum_{n=1}^{\bar{N}} \int d\mathbf{r} z |w_n(\mathbf{r})|^2 = 2 \frac{a}{2\pi} \gamma, \quad (11)$$

$$\gamma = i \sum_{n=1}^{\bar{N}} \int_0^{2\pi/a} dk \langle u_{nk} | u'_{nk} \rangle. \quad (12)$$

The multiband Berry phase γ is defined modulo 2π ;³⁵ hence the electronic term in p_0 is quantized modulo an integer times a , in agreement with our previous considerations. The nuclear term in p_0 is trivially quantized in the same way when, e.g., the origin is displaced. One can recognize in the right-hand side (rhs) of Eq. (12) the integral of Blount's expression³⁴ for the dipole operator in periodic systems. We notice that, while such formal expression is known since the 1960s, its relationship with the (spontaneous) polarization in

solids became clear only 30 years later, with the advent of the modern theory, based on the Berry phase.⁶⁻⁸

We adapt Eq. (12) to the case where the Bloch orbitals are expanded over a local basis set $\chi_{\mu}^l(\mathbf{r})$, where l is a cell index and μ is a basis index in the cell, with $1 \leq \mu \leq M$:

$$\varphi_{nk} = \sum_{l=-\infty}^{\infty} \sum_{\mu=1}^M \chi_{\mu}^l(\mathbf{r}) C_{\mu n}(k) e^{ikla} \quad (13)$$

and φ_{nk} are normalized over the 1D unit cell. In turn $u_{nk}(\mathbf{r})$, i.e., the cell periodic part of φ_{nk} [see Eq. (4)], is represented as

$$u_{nk}(\mathbf{r}) = \sum_{l=-\infty}^{\infty} \sum_{\mu=1}^M \chi_{\mu}^l(\mathbf{r}) C_{\mu n}(k) e^{ik(la-z)}. \quad (14)$$

In order to address the Berry phase and the Wannier centers, Eqs. (7) and (8), we need the k derivative.

$$u'_{nk}(\mathbf{r}) = i \sum_{l=-\infty}^{\infty} \sum_{\mu=1}^M (la-z) \chi_{\mu}^l(\mathbf{r}) C_{\mu n}(k) e^{ik(la-z)} + \sum_{l=-\infty}^{\infty} \sum_{\mu=1}^M \chi_{\mu}^l(\mathbf{r}) C'_{\mu n}(k) e^{ik(la-z)}. \quad (15)$$

Then the scalar product is

$$i \langle u_{nk} | u'_{nk} \rangle = \sum_{l=-\infty}^{\infty} \sum_{\mu, \nu=1}^M e^{ikla} C_{\mu n}^*(k) C_{\nu n}(k) \int d\mathbf{r} \chi_{\mu}^0(\mathbf{r}) (z-la) \chi_{\nu}^l(\mathbf{r}) + i \sum_{l=-\infty}^{\infty} \sum_{\mu, \nu=1}^M e^{ikla} C_{\mu n}^*(k) C'_{\nu n}(k) \int d\mathbf{r} \chi_{\mu}^0(\mathbf{r}) \chi_{\nu}^l(\mathbf{r}). \quad (16)$$

We now switch to a compact notation defining $S_{\mu\nu}^{0l}$ as the overlap between basis function μ in cell 0 and ν in cell l , and $Z_{\mu\nu}^{0l}$ as the corresponding dipole matrix element:

$$S_{\mu\nu}^{0l} = \int d\mathbf{r} \chi_{\mu}^0(\mathbf{r}) \chi_{\nu}^l(\mathbf{r}),$$

$$Z_{\mu\nu}^{0l} = \int d\mathbf{r} \chi_{\mu}^0(\mathbf{r}) z \chi_{\nu}^l(\mathbf{r}), \quad (17)$$

$$i \langle u_{nk} | u'_{nk} \rangle = \sum_{\mu, \nu=1}^M C_{\mu n}^*(k) C_{\nu n}(k) \sum_{l=-\infty}^{\infty} e^{ikla} (Z_{\mu\nu}^{0l} - la S_{\mu\nu}^{0l}) + i \sum_{\mu, \nu=1}^M C_{\mu n}^*(k) C'_{\nu n}(k) \sum_{l=-\infty}^{\infty} e^{ikla} S_{\mu\nu}^{0l}. \quad (18)$$

We notice that the infinite lattice sums of the overlap and dipole matrix terms are absolutely (and fast!) convergent, due to the locality of the basis set. We also notice that the complex $C(k)$ coefficients are arbitrary by a k -dependent phase factor $e^{i\alpha(k)}$, which contributes to their k derivative: the choice of such phase is referred to as to the choice of the gauge. For example, the analytical approach of Pople *et al.*³⁶ for orbital derivatives $C'(k)$ as applied by Champagne and Andre³⁷ corresponds indeed to the specific gauge choice (so-

called parallel transport) where the overlap between the orbitals at k and $k+\Delta k$ is taken as real (and positive).

Here instead we are going to adopt a finite-difference approach, by adopting the most general gauge, with the only constraint that φ_{nk} is periodic in k with period $2\pi/a$ (so-called periodic gauge). From Eq. (14) it follows that the C coefficients are periodic as well:

$$C_{\mu\nu}\left(k + \frac{2\pi}{a}\right) = C_{\mu\nu}(k). \quad (19)$$

Even by adopting such a constraint, substantial arbitrariness remains. First, different gauges may lead to *underlying* Wannier orbitals [see Eqs. (6) and (7)] which are displaced by an integer multiple of a , similar to translations in a system of integer point charges. In principle, this could be fixed by choosing the origin of the unit cell and imposing that all the $l=0$ Wannier orbitals are centered in the $l=0$ unit cell: $0 \leq \bar{z}_{\mu\nu 0} < a$. However, we recall that no actual localization is carried out when working with Eq. (12) [and then Eq. (18)], and so correcting the implicit Wannier orbital centers in this way is not possible. Regardless, the physical properties of the infinite system *must not* depend on such origin choice or, more generally, on *any* gauge choice. Second, different gauges lead to Wannier orbitals which have quite different localization properties;³⁸ Marzari and Vanderbilt have shown³² how to choose the preferred gauge where the Wannier orbitals possess optimal localization according to Boys's criterion.

Ultimately, most of the gauge arbitrariness disappears after Eq. (18) is integrated over the reciprocal cell $[0, 2\pi/a)$; only modulo 2π arbitrariness survives, leading to a p_0 which is arbitrary modulo a .

Then, similar to the system of integer point charges, Eq. (10), the cell dipole p_0 , reads in the spin-unpolarized case:

$$p_0 = p_{0,\text{nuc}} - 2 \sum_{n=1}^{\bar{N}} \bar{z}_{n0} = p_{0,\text{nuc}} - 2 \frac{a}{2\pi} \gamma, \quad (20)$$

$$\begin{aligned} \gamma &= \sum_{n=1}^{\bar{N}} \sum_{\mu,\nu=1}^M \int_0^{2\pi/a} dk C_{\mu\nu}^*(k) C_{\nu\mu}(k) \sum_{l=-\infty}^{\infty} e^{ikla} (Z_{\mu\nu}^{0l} - la S_{\mu\nu}^{0l}) \\ &+ i \sum_{n=1}^{\bar{N}} \sum_{\mu,\nu=1}^M \int_0^{2\pi/a} dk C_{\mu\nu}^*(k) C'_{\nu\mu}(k) \sum_{l=-\infty}^{\infty} e^{ikla} S_{\mu\nu}^{0l} \\ &= \gamma_1 + \gamma_2, \end{aligned} \quad (21)$$

where $p_{0,\text{nuc}}$ is the nuclear contribution to the cell dipole. Equations (20) and (21) are not new in the quantum-chemistry literature,^{4,20,22,23} where they have been used over the years in evaluating dipole *derivatives*, typically with respect to a macroscopic longitudinal electric field E , for systems as large as carbon nanotubes.^{39,40} In fact, it has been shown^{22,23} that the first derivative of Eq. (20) with respect to E leads essentially to the time-honored Genkin-Mednis formula.¹ Higher order derivatives have been addressed in more recent times: while the first attempts were controversial,^{18,19} the work of Ref. 4 has gone unchallenged and opened new avenues for the study of nonlinear polariz-

abilities of polymers.⁵ Only recently Eq. (20) has also been used in order to address the dipole itself and related to the modern theory of polarization.^{21,24}

IV. DISCRETIZATION ALGORITHM

We split the multiband Berry phase, Eqs. (12) and (21), as follows:

$$\gamma = i \sum_{n=1}^{\bar{N}} \int_0^{2\pi/a} dk \langle u_{nk} | u'_{nk} \rangle = \gamma_1 + \gamma_2, \quad (22)$$

where the subscripts 1 and 2 refer to the first and second lines of Eq. (21), respectively. In numerical implementations, the k integration is discretized: the first line (γ_1) of Eqs. (18) and (21) is gauge-invariant point by point and can be trivially discretized, while care has to be taken about the second line (γ_2), where a k -dependent phase factor contributes to the integrand. A rather involved way of getting rid of such phase factors has been demonstrated in Refs. 24 and 25.

At variance with the previous quantum-chemistry literature we present a discretization algorithm which is numerically gauge invariant in form. In this aspect, our method is equivalent to the one currently implemented in the electronic-structure codes for crystalline solids, based on either a plane-wave basis set^{13,16,17} or local basis sets.^{14,15} With respect to the latter implementations, however, the present algorithm has a notable advantage. Specifically, it incorporates the local basis set in a more direct and native way and requires evaluation of simpler matrix elements: in fact, the basic ingredients are the standard dipole $Z_{\mu\nu}^{0l}$ and overlap $S_{\mu\nu}^{0l}$ matrix elements, Eq. (17), while the current CRYSTAL implementation²⁷ requires the evaluation of plane-wave matrix elements.

We start by defining the $M \times M$ overlap matrix (where M is the number of basis functions in the unit cell)

$$S_{\mu\nu}(k) = \sum_{l=-\infty}^{\infty} e^{ikla} S_{\mu\nu}^{0l}, \quad (23)$$

and we rewrite γ_2 as

$$\begin{aligned} \gamma_2 &= i \int_0^{2\pi/a} dk \sum_{n=1}^{\bar{N}} \sum_{\mu,\nu=1}^M C_{\mu\nu}^*(k) S_{\mu\nu}(k) C'_{\nu\mu}(k) \\ &= i \int_0^{2\pi/a} dk \text{tr} \left\{ C^\dagger(k) S(k) \frac{d}{dk} C(k) \right\} \\ &= -\text{Im} \int_0^{2\pi/a} dk \text{tr} \left\{ C^\dagger(k) S(k) \frac{d}{dk} C(k) \right\}. \end{aligned} \quad (24)$$

Next, it is expedient to define the $\bar{N} \times \bar{N}$ matrix (where \bar{N} is the number of occupied bands)

$$\Sigma(k, k') = C^\dagger(k) S(k) C(k'), \quad (25)$$

which coincides with the identity for $k'=k$. Note that only k' is a variable, while k is a fixed parameter. Using the—well known from linear algebra—matrix identity

$$\det \exp A = \exp \operatorname{tr} A \quad (26)$$

and identifying $A = \ln \Sigma$, one readily gets

$$\operatorname{tr} \left\{ \Sigma^{-1}(k, k') \frac{d}{dk'} \Sigma(k, k') \right\} = \frac{d}{dk'} \ln \det \Sigma(k, k'), \quad (27)$$

which for $k' = k$ coincides with the integrand in Eq. (24). We are now ready to discretize. From Eq. (27) we have

$$\left. \frac{d}{dk'} \ln \det \Sigma(k, k') \right|_{k'=k} \simeq \frac{1}{\Delta k} \ln \det \Sigma(k, k + \Delta k). \quad (28)$$

It is worth noticing that the left-hand side of Eq. (28) implies a differentiable Σ , while instead the rhs is built of eigenvalues at different k 's, according to Eq. (25), which contain arbitrary, possibly erratic, phase factors. As shown below, a major virtue of the present discretization algorithm is the irrelevance of such phase factors. At variance with the approach of Refs. 24 and 25, here there is no need of getting rid of them.

With the above transformations, γ_2 is then approximated as

$$\gamma_2 \simeq -\operatorname{Im} \frac{1}{\Delta k} \int_0^{2\pi/a} dk \Sigma(k, k + \Delta k). \quad (29)$$

Suppose we diagonalize either the Fock operator or the KS Hamiltonian over a regular mesh of $N_p k$ points

$$k_j = \frac{2\pi}{a} \frac{j}{N_p}, \quad j = 1, N_p, \quad (30)$$

spaced by $\Delta k = 2\pi/(N_p a)$. The discretization of the integral in Eq. (29) yields

$$\begin{aligned} \gamma_2 &\simeq -\operatorname{Im} \sum_{j=1}^{N_p} \ln \det \Sigma(k_j, k_{j+1}) \\ &= -\operatorname{Im} \ln \prod_{j=1}^{N_p} \det \Sigma(k_j, k_{j+1}) \\ &= -\operatorname{Im} \ln \prod_{j=1}^{N_p} \det C^\dagger(k_j) S(k_j) C(k_{j+1}). \end{aligned} \quad (31)$$

Each of the factors in the product is a complex number, whose modulus approaches 1 when the mesh becomes dense; notice that the last factor in the product involves the point k_{N_p+1} , which is outside the integration domain $[0, 2\pi/a)$: this point must then be replaced by k_1 , owing to the periodic-gauge condition, Eq. (19).

The “ $\operatorname{Im} \ln$ ” amounts to extracting the phase (part of the full Berry phase) of the product of determinants in Eq. (31). Suppose the diagonalization routine assigns an arbitrary phase to the eigenstates at a given k_j or, in the case of degeneracy, even a unitary mixing $U(k_j)$, with

$$\det U(k_j) = e^{i\vartheta_j}. \quad (32)$$

Then, according to Eq. (25), the new $\bar{\Sigma}$ is

$$\bar{\Sigma}(k_j, k_{j+1}) = U^\dagger(k_j) \Sigma(k_j, k_{j+1}) U(k_{j+1}), \quad (33)$$

where U 's are arbitrary. It follows that

$$\det \bar{\Sigma}(k_j, k_{j+1}) = e^{-i\vartheta_j} [\det \Sigma(k_j, k_{j+1})] e^{i\vartheta_{j+1}}, \quad (34)$$

and the ϑ 's are arbitrary phases from the diagonalization procedure. It is easily realized that such phases have no effect on the product in Eq. (31), since therein they always appear in pairs with \pm signs.

The presence of the overlap matrix in Eq. (31) is the only substantial difference of the nonorthogonal local basis set expression compared to the plane-wave case. Such overlap matrix between neighboring k points has already been encountered earlier, for example, in the approach to establish band continuity and resolve crossings in k space.⁴¹ The form of Eq. (31) shows asymmetry, since one set of orbital coefficients and the overlap matrix are taken at point k_j , while the second set of orbital coefficients comes from point k_{j+1} . Here, instead we suggest using the overlap matrix from the midpoint

$$\gamma_2 \simeq -\operatorname{Im} \ln \prod_{j=1}^{N_p} \det C^\dagger(k_j) S\left(k_j + \frac{\Delta k}{2}\right) C(k_{j+1}). \quad (35)$$

Such $S(k_j + (\Delta k/2))$ overlap matrices are easy to generate on the fly from the direct space overlap elements. Overall, this midpoint choice has two advantages. First, one could carry out an analysis and show that for a given k space grid the modulus of each individual determinant in Eq. (35) is closer to 1 compared to the determinants in Eq. (31). Second, if the k space grid is symmetric with respect to the Γ point (and it usually is), and the orbital coefficients only for nonredundant k points are computed, then one can show that

$$\begin{aligned} \det C^\dagger(k_j) S\left(k_j + \frac{\Delta k}{2}\right) C(k_{j+1}) \\ = \det C^\dagger(-k_{j+1}) S\left(-k_j - \frac{\Delta k}{2}\right) C(-k_j). \end{aligned} \quad (36)$$

So by utilizing this property roughly half of all the determinants along a closed cyclic path can be obtained from the symmetry considerations and need not be explicitly computed, in contrast to Eq. (31).

Since the imaginary part of the logarithm of a complex number is defined modulo 2π , γ_2 leads to a unit-cell dipole p_0 which is defined modulo a . Instead, the dipole per cell p of any finite chain is an unambiguous quantity. Nonetheless—owing to an important theorem⁴²—in the long-chain limit p must be equal to one of the quantized values of p_0 : which one? This depends on the chemical nature of the system: we are going to address this and similar issues in a subsequent publication.

For 2D and 3D periodic systems the Berry phase [Eqs. (31) and (35)] is computed along all closed paths of the form $\{k_j, k_b, k_c\} \rightarrow \{k_{j+1}, k_b, k_c\}$ for a given reciprocal space direction, with the final value obtained by averaging the values for each $[k_j \rightarrow k_{j+1}]$ path on the 2D plane $\{\dots, k_b, k_c\}$.

V. HIGHER ORDER DERIVATIVES OF THE PERIODIC DIPOLE

Equations (31) and (35) are derived based on the discretized k space derivative operator as per Eq. (29), i.e.,

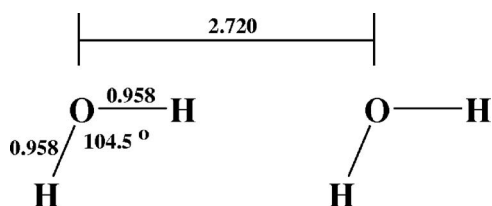


FIG. 1. 1D-periodic water chain. In the notation $[\cdots(\text{H})-\text{O}-\text{H}\cdots]$ the (H) atom is the one that is below oxygen. The distances are given in Å.

$\Delta/\Delta k$, instead of d/dk . Depending on the situation, one may or may not be concerned about the discrepancies between the two choices. Naturally, as the spacing between the k points decreases, both approaches converge to the same answers.

For example, when working with the derivatives of the dipole moment with respect to the electric field one can conveniently compute polarizability and higher order hyperpolarizabilities entirely via the analytic d/dk derivatives of the orbitals.^{20,24} Since properly applying finite electric fields to the periodic systems and obtaining the value of Eq. (22) for a nonzero field are rather difficult tasks, one may not actually care about obtaining the derivatives which would match the numerical derivatives of Eq. (22) in a finite field. Some further comment about *finite* versus *infinitesimal* fields is provided below (final paragraph of this paper).

On the other hand, numerical derivatives with respect to the atomic displacements at fixed a (i.e., the infrared charge tensors, also known as Born charge tensors) are much more computationally accessible, in the sense that one could readily displace the atoms and numerically differentiate Eq. (22). We further mention that even derivatives with respect to a (analog of piezoelectricity in condensed matter) can be dealt with by means of the Berry phase approach.^{6,8}

For full consistency with the numerical differentiation, in analytical schemes one should use the “perturbation expansion after discretization” approach suggested by Nunes and Gonze in Ref. 43 and implemented by Sai *et al.*⁴⁴ In the quantum-chemistry literature, Jacquemin *et al.* proceeded by a similar route,²⁵ when exactly differentiating the expressions for the periodic dipole given in Ref. 24. Overall, for an extensive discussion of the differences between the fully analytic and partially discretized derivatives we refer the reader to Ref. 44.

VI. BENCHMARKS

The actual expressions, Eqs. (31) and (35), were coded in GAUSSIAN 03 (Ref. 45) and relied on the periodic boundary condition implementation of Kudin and Scuseria.⁴⁶ As a test case we use the chain of water molecules from Ref. 20, with

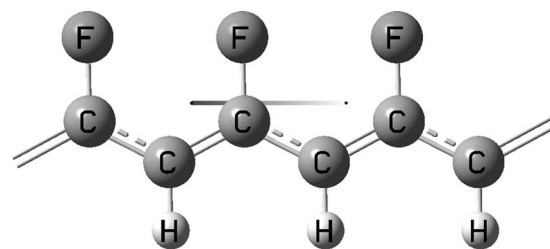


FIG. 2. 1D-periodic fluorinated *trans*-polyacetylene $[\cdots\text{CHCF}\cdots]$. Three unit cells are shown for clarity, and the translation vector is indicated by the horizontal line over the central cell ($a=2.47132$ Å). The bond distances and angles are $r(\text{C}=\text{C})=1.363$ Å, $r(\text{C}-\text{C})=1.428$ Å, $r(\text{C}-\text{H})=1.09$ Å, $r(\text{C}-\text{F})=1.339$ Å, $\alpha(\text{CCC})=124.6^\circ$, $\alpha(\text{C}=\text{C}-\text{F})=117.0^\circ$, and $\alpha(\text{C}=\text{C}-\text{H})=117.0^\circ$.

the same method and basis set (BLYP/STO-3G), shown in Fig. 1. This is a convenient system since it allows one to place the cell boundaries at different locations and thus redistribute the contributions between γ_1 and γ_2 . What is interesting in Table I is how the individual terms vary with the boundaries, yet end up yielding the same total polarization (modulo a). In Ref. 21 this first term (γ_1) was referred to as the “intracellular” polarization, while the second (γ_2) as “intercellular” polarization. Since the cell boundary is arbitrary, such partition is arbitrary as well: only the sum of the two terms is relevant. A further arbitrariness apparently remains, since even the sum $\gamma_1 + \gamma_2$ *does* depend on the origin choice within the cell: as discussed in Ref. 8 this latter arbitrariness is removed when considering the nuclear and electronic terms altogether. We also comment that Eq. (26) in Ref. 20 represents only $p(\gamma_1)$, while Table III of the same reference contains $p(\gamma_1)$ values for different periodic cell boundaries in the water chain.

Our second example is a fully conjugated fluorinated *trans*-polyacetylene $[\cdots\text{CHCF}\cdots]$ shown in Fig. 2. The fluorine atom has been added in order to remove the inversion center and make the dipole nonzero.⁴⁷ The calculations have been carried out at the restricted Hartree-Fock level with the STO-3G basis set. Table II contains the longitudinal dipole moment differences for several pairs of finite size oligomers, the polynomial extrapolation of these values to infinity identical to the approach discussed in Ref. 48 for polarizabilities, and finally, the periodic dipole obtained with the presented here Berry phase algorithm. One can observe that the match between the extrapolated and the fully periodic value of the dipole moment is excellent, confirming both the high accuracy of the physically justified polynomial interpolation and the novel periodic Berry phase approach.

An important practical question is what is the convergence rate of the orbital phase contribution γ_2 from Eq. (22)

TABLE I. Periodic dipole contributions (in a.u.) for a chain of water molecules (Fig. 1). One of the OH bonds is aligned with the periodic direction, and the cell boundaries are placed at different locations. In our notation, the noncovalent spacing is indicated by double dots. The periodic vector $a = 5.140057$ a.u. = 2.72 Å, $N_k = 16384$. The oligomer p_{tot} value from Ref. 20 is 0.734033 a.u.

System	$p_{\text{elec}}(\gamma_1)$	$p_{\text{nuc}}(\gamma_1)$	$p(\gamma_1)$	$p(\gamma_2)$	p_{tot}	P_{tot}
$\cdots(\text{H})-\text{O}-\text{H}\cdots$	-0.912721	1.357080	0.444360	0.289679	0.734038	0.734038
$-\text{O}-\text{H}\cdots(\text{H})-$	-5.216644	6.497135	1.280491	4.593602	5.874094	0.734037 + a
$-\text{H}\cdots(\text{H})-\text{O}-$	-48.303270	47.617576	0.685694	-3.720323	-4.406017	0.734040 - a

TABLE II. Dipole moment values for fluorinated *trans*-polyacetylene (in a.u.). The polynomial extrapolation based on the last two oligomer values as per Ref. 48 yielded the equation $[p(n \rightarrow \infty) = 0.872\,756 - 3.251\,50/n^2]$. For the Berry phase calculation $p(\gamma_1) = -0.158\,916$, $p(\gamma_2) = 1.031\,668$.

Calculation	P_{tot}
65-64	0.871 922
97-96	0.872 404
129-128	0.872 561
193-192	0.872 669
∞ (extrapolated)	0.872 756
∞ (Berry phase)	0.872 752

with the size of the k space grid? It is instructive to investigate both the imaginary part as in Eqs. (31) and (35), and the norm of the entire product. The log-log plot of the difference with respect to the converged modulus of 1 as well as to the phase value for infinitely dense grid of k points is given in Fig. 3. There, one can clearly see that irrespective of the overlap matrix choice, the leading error for the phase factor goes as Δk^2 , while the norm approaches 1 only as Δk . Quite notably, Eq. (35) with the midpoint overlap matrices yields numbers which are closer to the converged values for a given k space mesh.

We briefly digress at this point on the subject of the above norm, or equivalently, the real part of the logarithm in Eqs. (31) and (35). This is a basic ingredient in the modern theory of localization;^{49,50} indeed, the coefficient of the term linear in Δk , heuristically found in Fig. 3, governs the localization of the Wannier functions. More precisely, such coefficient yields the minimum quadratic spread (otherwise known as second moment) of the Wannier orbitals in the z direction, averaged over the cell: see, e.g., Eqs. (11) and (12) in Ref. 49.

VII. CONCLUSIONS

We provide here some important clarifications about the dipole per cell of long polymeric chains in the HF and KS cases. The hallmark and the novelty of the present formula-

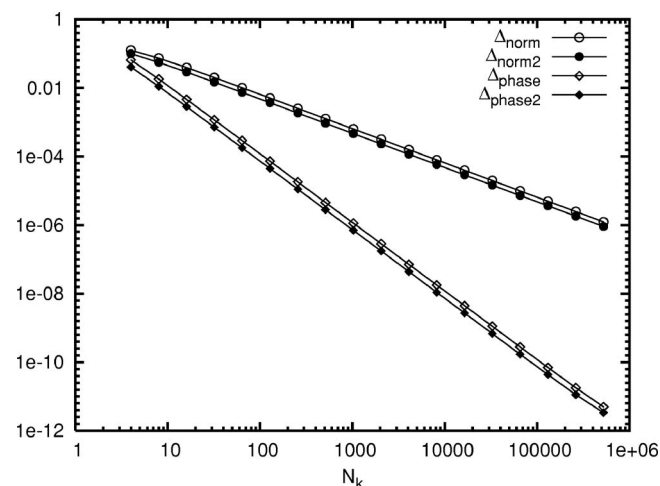


FIG. 3. Log-log plot of the difference for the norm and phase from Eq. (31) (labeled Δ_{norm} , Δ_{phase}) and from Eq. (35) (labeled $\Delta_{\text{norm}2}$, $\Delta_{\text{phase}2}$) from their respective converged limits for the $[\cdots(\text{H})-\text{O}-\text{H}\cdots]$ configuration.

tion are—with respect to the published quantum-chemistry literature—the dominant roles played by localized orbitals (Boys type and Wannier), which allow us to relate finite and infinite chains in a very natural way. It is only as a second step that we proceed to k space formulation, where the concept of Berry phase arises quite naturally as the way to compute the Wannier orbital positions. We also introduce and benchmark a novel algorithm for the evaluation of such Berry phases when the Bloch orbitals are expressed in terms of nonorthogonal local basis functions.

Our expression for the dipole per cell, Eqs. (20) and (21), addresses the “dipole itself” (per cell) and is the starting point for evaluating dipole derivatives (and *finite differences*) in the presence of noncentrosymmetric perturbations. We first notice that it is mandatory to consider the nuclear and electronic charge altogether, given that charge neutrality is essential when dealing with dipoles; we further notice that even ensuring charge neutrality, care has to be taken in relating the dipole of a unit cell p_0 , as defined in Eqs. (20) and (21), to physical (and measurable) properties of a *finite* chain. Still p_0 is the basic ingredient for evaluating the dipole of quasi-1D stereoregular system in the long-chain limit, but in general p_0 need *not* to be equal to the dipole per cell of the finite chain: actually, it may differ from it by an integer times the lattice constant a . As we demonstrate in more detail elsewhere,⁴⁷ this fact has much to do with the “quantization of surface charge,” well known in surface physics.⁴²

Finally, we briefly comment about the case where an electric field E is applied to the chain. For a *finite* field E (along z) Eqs. (20) and (21) cannot be acritically used. In fact the field operator Ez breaks the translational invariance of the unperturbed Hamiltonian; hence the eigenstates no longer enjoy the Bloch form. Nonetheless Eqs. (20) and (21) can be legitimately used to evaluate *derivatives* with respect to E at $E=0$. The apparent paradox is solved by noticing that the problem (and the spectrum) is *nonanalytic* at $E=0$; hence the derivatives at $E=0$ and the case $E \neq 0$ deserve a separate treatment. The latter case can be dealt with by adopting either a time-independent non-Hamiltonian formulation^{28,29} or a time-dependent Hamiltonian formulation;^{4,26,51} the former addresses a metastable state (resonance), while the latter is based on switching to a vector-potential gauge.

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