

Longitudinal polarizability of long polymeric chains: Quasi-one-dimensional electrostatics as the origin of slow convergence

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The longitudinal linear polarizability $\alpha(N)$ of a stereoregular oligomer of size N is proportional to N in the large- N limit, provided the system is nonconducting in that limit. It has long been known that the convergence of $\alpha(N)/N$ to the asymptotic α_∞ value is slow. We show that the leading term in the difference between $\alpha(N)/N$ and α_∞ is of the order of $1/N$. The difference $[\alpha(N) - \alpha(N-1)]$, as well as $\alpha_{\text{center}}(N)$ (when computationally accessible), also converge to α_∞ , but faster, the leading term being of the order of $1/N^2$. We also present evidence that in these cases the power law convergence behavior is due to quasi-one-dimensional electrostatics, with one exception. Specifically, in molecular systems the difference between $\alpha(N)/N$ and α_∞ has not just one but two sources of the $\mathcal{O}(1/N)$ term, with one being due to the aforementioned Coulomb interactions, and the second due to the short ranged exponentially decaying perturbations on chain ends. The major role of electrostatics in the convergence of the remainders is demonstrated by means of a Clausius–Mossotti-type classical model. The conclusions derived from the model are also shown to be applicable in molecular systems, by means of test-case *ab initio* calculations on linear stacks of H_2 molecules, and on polyacetylene chains. The implications of the modern theory of polarization for extended systems are also discussed. © 2005 American Institute of Physics.

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I. INTRODUCTION

Quasi-one-dimensional systems have a microscopic size in the xy coordinates, while their length along z is in principle macroscopic. If a system in this class is nonconducting and macroscopically homogeneous, its longitudinal linear polarizability is an extensive quantity. This means that the dipole linearly induced along z by an applied unit field parallel to z is asymptotically proportional to the length of the system. Ergo, the polarizability per unit length is an intensive quantity and goes to finite limit. The main issue addressed by the present work is how and why the asymptotic value is approached.

Several authors have investigated from first principles the linear polarizability of long polymeric chains.^{1–5} It was heuristically found that asymptotic convergence is often slow,^{6–8} with slowness depending on the computational techniques, e.g., Hartree–Fock (HF), density-functional theory (DFT), or correlated-wave function methods.^{9–12} Other studies have investigated the same issue on the basis of tight-binding model Hamiltonians.^{13–15} However, a systematic investigation on how slow the convergence is, and why it is slow, is basically lacking. In this work we aim to fill this gap. Our results provide understanding as a matter of principle,

while at the same time suggesting a practical extrapolation formula whose physical root is in quasi-one-dimensional electrostatics.

In the following we focus on systems which are “crystalline” (or stereoregular) in the z direction, i.e., obtained as a one-dimensional stack of microscopic monomers (unit cells), all identical except possibly at the two stack’s ends. If we call $\alpha(N)$ the longitudinal linear polarizability of the oligomer of size N , the asymptotic polarizability per unit cell α_∞ can be defined either as $\alpha(N)/N$ or as $\alpha(N) - \alpha(N-1)$, in the limit of large N . Here we show that the convergence of $\alpha(N)/N$ to α_∞ is governed by end effects, due to both electrostatics and quantum mechanics, both yielding $1/N$ rate of convergence. In contrast, the convergence of $\alpha(N) - \alpha(N-1)$ to α_∞ is attributable entirely to the peculiarity of electrostatics in quasi-one-dimensional systems and has a universal power-law behavior of $1/N^2$, independent of the computational techniques adopted. These slow power-law convergences are peculiar to quasi-one-dimensional electrostatics: we stress that three-dimensional systems are quite different in this respect. In fact the dielectric constant of a crystalline solid can be actually evaluated by computing the polarizability of a *few-layer* slab.^{16,17} The peculiar convergence laws in quasi-one-dimensional systems have been sel-

dom noticed in the literature, one notable exception being a paper by Léonard and Tersoff¹⁸ on nanotubes.

We are going to study in detail two test cases: linear stacks of H₂ molecules, and a paradigmatic conjugated polymer such as transpolyacetylene, with conjugated double bonds. Our test cases are addressed by means of both HF and DFT [using the Becke–Lee–Yang–Parr (BLYP, Ref. 19) functional]. Polyacetylene is notoriously a very challenging case for the most common functionals,^{9,10} including BLYP. However, we stress that the aim of the present work is providing *qualitative* understanding of the large- N behavior, *not* quantitatively accurate values. For the same reason, we limit ourselves to the use of very simple basis sets allowing us to look at oligomers of large sizes.

II. A CLASSICAL MODEL SYSTEM

It is expedient to start with a simple classical model system, which is the one-dimensional analog of the time-honored Clausius–Mossotti model.²⁰ Suppose we have a one-dimensional stack of N equally spaced and identical localized charge distributions (Fig. 1), having linear polarizability $\alpha(1)$. In the limit where the dimensions of the localized charge can be considered pointlike with respect to the nearest-neighbor distance b , the i th charge distribution acquires an induced dipole moment μ_i , equal to $\alpha(1)$ times the *local* electric field at site i . Such field is the sum of the “bare” external applied field $F^{(\text{ext})}$ and of the induced field $F_i^{(\text{ind})}$ due to the other induced dipoles μ_j . The relevant equations are

$$F_i^{(\text{ind})} = \frac{2}{b^3} \sum_{j \neq i} \frac{\mu_j}{|i-j|^3}, \quad (1)$$

$$\mu_i = \alpha(1)F^{(\text{ext})} + \frac{2\alpha(1)}{b^3} \sum_{j \neq i} \frac{\mu_j}{|i-j|^3}. \quad (2)$$

The self-consistent problem amounts therefore to a system of N linear equations in the unknowns μ_i . Upon defining for a given size N the local polarizability as

$$\alpha_i(N) = \mu_i/F^{(\text{ext})}, \quad (3)$$

the polarizability of the whole system is

$$\alpha(N) = \sum_i \alpha_i(N). \quad (4)$$

In the limit of an infinite stack the problem admits a simple analytic solution. All μ_i 's being equal, the dipole at site 0 can be written as

$$\mu_0 = \alpha(1)F^{(\text{ext})} + \frac{2\alpha(1)}{b^3} \sum_{j \neq 0} \frac{\mu_0}{|j|^3}, \quad (5)$$

where now the sum index runs between $-\infty$ and ∞ . A simple inversion gives therefore²¹

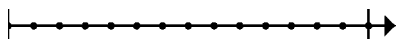


FIG. 1. A one-dimensional stack of N polarizable charge distributions ($N = 15$ here). Within the extreme Clausius–Mossotti model, the distributions are assumed as pointlike.

$$\mu_0 = \alpha(1)F^{(\text{ext})} \left[1 - \frac{4\alpha(1)}{b^3} \zeta(3) \right]^{-1}, \quad (6)$$

where ζ is the Riemann zeta function, with $\zeta(3) = 1.202\,056\,903$. The polarizability per unit cell $\alpha_\infty = \alpha_0(\infty)$ is therefore according to Eq. (6),

$$\alpha_\infty = \left[\frac{1}{\alpha(1)} - \frac{4}{b^3} \zeta(3) \right]^{-1}. \quad (7)$$

The above expression is indeed the exact analog of the Clausius–Mossotti formula—popularly known for a three-dimensional cubic system—for the case of a linear system.

The central issue of the present work is how the local polarizabilities $\alpha_i(N)$ in a finite stack converge to α_∞ . Each dipole creates an electric field that goes as the inverse third power of distance. If one were to truncate an infinite chain of *identical dipoles* to a semifinite one on one of the ends, the overall effect of excluded dipoles on a given site would be proportional to

$$\sum_{j=i+M}^{\infty} \frac{1}{|i-j|^3} = \sum_{k=M}^{\infty} \frac{1}{|k|^3} = O(1/M^2), \quad (8)$$

where M is the number of sites between a given site i and the truncation point. Additionally, we have to consider the fact that the induced dipoles μ_i differ from their asymptotic value $\alpha_\infty F^{(\text{ext})}$, as well as other self-consistency effects; these additional effects are $O(1/M^2)$ as well.²²

We start by keeping the two leading orders, thus approximating all truncation effects as a constant times M^{-2} plus another constant times M^{-3} . Considering the two ends of a stack of size N , the truncation effects on the i th polarizability lead to

$$\alpha_i(N) \simeq \alpha_\infty - \frac{e_2}{i^2} - \frac{e_2}{[(N+1)-i]^2} - \frac{e_3}{i^3} - \frac{e_3}{[(N+1)-i]^3}. \quad (9)$$

We may easily solve the linear system in Eq. (2), where self-consistency effects are automatically included: using then e_2 and e_3 as fitting parameters, the accuracy of the approximate expansion, Eq. (9), can be explicitly verified. This is shown in Fig. 2 for $N=129$: the match looks excellent for the most part of the curve, with the exception of the units close to the chain ends.

Keeping from now on only the leading term in Eq. (9), the total polarizability for the entire chain can be approximated by

$$\begin{aligned} \alpha(N) &\simeq \sum_{i=1}^N \left(\alpha_\infty - \frac{e_2}{i^2} - \frac{e_2}{[(N+1)-i]^2} \right) \\ &= N\alpha_\infty - 2e_2 \sum_{i=1}^N \frac{1}{i^2} = N\alpha_\infty - \text{const} + \frac{2e_2}{N}. \end{aligned} \quad (10)$$

The deviations on the chain ends, not considered in Eqs. (8) and (9), give rise to another $O(1)$ term in $\alpha(N)/N$. Considering both effects altogether we write the leading terms of $\alpha(N)/N$ as

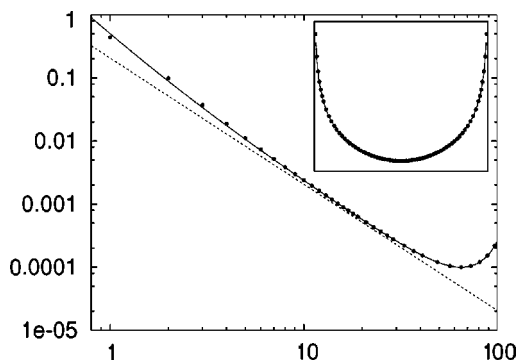


FIG. 2. Log-log plot of the difference of α_∞ and the local polarizabilities per site $\alpha_i(N)$ for a stack of $N=129$ Clausius–Mossotti sites. $\alpha(1)=5.812$, whereas the asymptotic value $\alpha_\infty=5.6757$. Solid circles correspond to the actual CM values. The solid line represents the fit according to Eq. (9) while the dashed line is only one quadratic term from this fitting expression. The inset contains semilog plot of the CM values and the fit.

$$\alpha(N)/N = \alpha_\infty - e_1/N + 2e_2/N^2, \quad (11)$$

where e_1 is a positive constant. Equation (11) makes it very clear that the convergence of $\alpha(N)/N$ to α_∞ is $O(1/N)$. Another notable conclusion that follows from either Eq. (9) or Eq. (11) is

$$\alpha(N) - \alpha(N-1) \approx \alpha_\infty - 2e_2/N^2. \quad (12)$$

If instead we address the polarizability of the central site in a chain of length N , with N odd, Eq. (9) yields

$$\alpha_{\text{center}}(N) \approx \alpha_\infty - 8e_2/N^2. \quad (13)$$

We have therefore the remarkable result that both $\alpha(N) - \alpha(N-1)$ and $\alpha_{\text{center}}(N)$ differ by their asymptotic value α_∞ by $O(1/N^2)$ terms, and that furthermore such terms are in the fixed ratio 1:4.

In all cases, end effects decay only polynomially with the system size. In fact, the inverse-power-law decay with distance is a universal feature of phenomena dominated by the Coulomb interaction. The long range of the tail effects is at the root of the slow asymptotic convergence, and is an outstanding manifestation of quasi-one-dimensional electrostatics, where “surface” effects decay very slowly into the “bulk.” As already mentioned in the Introduction, three-dimensional systems behave quite differently.^{16,17}

We have verified the above analytical result by numerically solving the linear system, Eq. (2), for N up to 1000. The results are summarized in Fig. 3, indeed confirming in a very perspicuous way that the leading terms in the asymptotic convergence of $\alpha(N) - \alpha(N-1)$ and $\alpha_{\text{center}}(N)$ are both $O(1/N^2)$, with the former being four times smaller than the latter. The convergence of $\alpha(N)/N$ to α_∞ is much slower, only $O(1/N)$.

The Clausius–Mossotti-type system considered in this section is a highly idealized one, where the polarizable charge distributions are assumed as pointlike. Nonetheless we will show that, insofar as the asymptotic behavior of the linear polarizability is addressed, this model captures the main qualitative features of more realistic quasi-one-dimensional systems. Even when detailed features of a given system are accounted for by means of quantum-

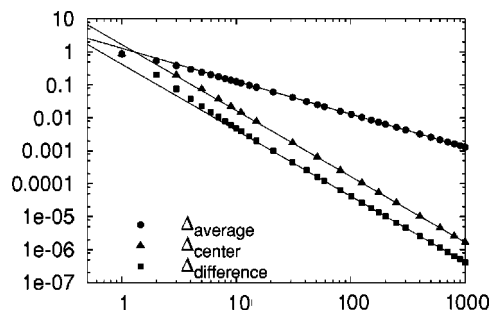


FIG. 3. One-dimensional Clausius–Mossotti-type model: asymptotic convergence of the linear polarizability per site as a function of N . We have used $\alpha(1)=5.812$ and $b=6$; only a sparse set of values of N is shown for the sake of clarity. $\Delta_{\text{average}} = \alpha_\infty - \alpha(N)/N$; $\Delta_{\text{center}} = \alpha_\infty - \alpha_{\text{center}}(N)$; $\Delta_{\text{difference}} = \alpha_\infty - \alpha(N) + \alpha(N-1)$. The slope of the straight lines in the logarithmic plot is -1 for Δ_{average} , and -2 for the other cases with the shift in the lines caused by a factor-of-four difference in prefactors.

mechanical first-principle calculations, the asymptotic behavior is dominated by the peculiarity of quasi-one-dimensional electrostatics.

III. SIMPLE QUANTUM-MECHANICAL SYSTEMS

We now address some simple oligomers, whose linear polarizability we study from first principles, both within HF and DFT. For the latter case, we have chosen to work with the BLYP functional.¹⁹ Most calculations have been performed with the GAUSSIAN98 code,²³ a few of them (specified below) with the GAMESS code.²⁴ Since the aim here is to focus on basic qualitative issues, we have chosen to adopt throughout a very simple basis set, namely, STO-3G. The linear polarizability has been evaluated analytically, using either coupled perturbed HF (CPHF) or coupled perturbed Kohn–Sham (CPKS) algorithms. Various thresholds in both programs were tightened up in order to achieve high accuracy in the computed values.

We study the polarizability as a function of size in: (1) stacks of N aligned H_2 molecules, at two selected intermolecular separations, and (2) transpolyacetylene chains $\text{C}_{2N}\text{H}_{2N+2}$. Both systems have been addressed before in the literature, and in particular for case (1) we reproduce some of the results of Ref. 5.

When considering the quantum system, we address the “local” polarizabilities $\alpha_i(N)$ by means of localized orbitals. In fact it has been shown long ago by Maestro and Moccia²⁵ that the CPHF polarizability of a closed-shell molecule can be decomposed into a sum of contributions from localized orbitals, using the Boys localization criterion.²⁶ We have performed such decomposition, implemented in the standard distribution of the GAMESS code,²⁴ for H_2 chains and even for transpolyacetylene. In the simple case of H_2 there is a single Boys orbital per H_2 molecule, centered in the bond region; therefore, we may take over Eq. (4) as it is, where we simply interpret the molecular polarizabilities $\alpha_i(N)$ as the polarizability of Boys orbitals. The central polarizability $\alpha_{\text{center}}(N)$, for odd N , is defined in the obvious way.

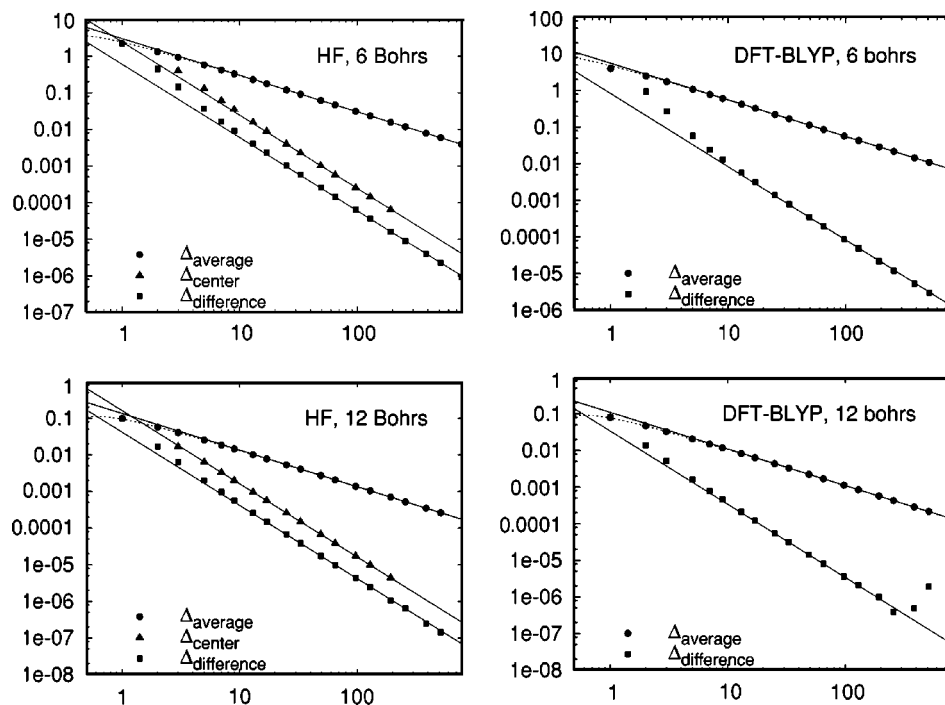


FIG. 4. First-principle longitudinal polarizabilities of chains of N H_2 molecules, within HF and DFT, for two different intermolecular separations. $\Delta_{\text{average}} = \alpha_\infty - \alpha(N)/N$; $\Delta_{\text{center}} = \alpha_\infty - \alpha_{\text{center}}(N)$; $\Delta_{\text{difference}} = \alpha_\infty - \alpha(N) + \alpha(N-1)$. The slope of the straight solid lines in the logarithmic plots is -1 for Δ_{average} and -2 for $\Delta_{\text{difference}}$. In the former case an expansion to the next leading term beyond the first is used for the actual fit (dashed lines).

A. Stacks of H_2 molecules

We have studied the longitudinal linear polarizability of up to 769 aligned H_2 molecules. The molecular bond length is set at 2 bohrs and two intermolecular (center-to-center) separations have been studied: 6 and 12 bohrs. The results, both CPHF and CPKS-BLYP, are all reported in Fig. 4 by means of log-log plots. The 6 bohrs geometry is identical to case “C” in Ref. 5. Within our basis set, the HF polarizability of an isolated H_2 molecule is $\alpha(1)=5.8122$, while the DFT-BLYP one is $\alpha(1)=5.2494$. All polarizability values are given in bohr.³

Several outstanding features emerge from the plots. First of all, there is no outstanding qualitative difference between HF and DFT: both approaches for large N lead to the same kind of asymptotic behavior. Second, the three quantities $\alpha(N)/N$, $\alpha(N) - \alpha(N-1)$, and $\alpha_{\text{center}}(N)$ tend to the same asymptotic limit α_∞ , the leading deviations being $O(1/N)$, $O(1/N^2)$, and $O(1/N^2)$ (in this order). Third, $\Delta_{\text{difference}}$ and Δ_{center} are precisely in the 1:4 ratio. Overall, the quantum system behaves exactly as the classical Clausius–Mossotti one-dimensional stack. In fact, we stress the main message of the present work: quasi-one-dimensional electrostatics and tail effects dominate the large- N qualitative behavior of longitudinal polarizability.

Our calculated asymptotic α_∞ values are: 8.0031 (HF, 6 bohrs); 9.2495 (DFT, 6 bohrs); 5.9103 (HF, 12 bohrs); and 5.3293 (DFT, 12 bohrs). These values were readily obtained by fitting a few $\alpha(N) - \alpha(N-1)$ differences for our largest N 's to the asymptotic formula. When we compare such α_∞ values to those provided by Eq. (7) we find for the 12 bohrs geometry that the agreement is within three parts in a thousand, while for the 6 bohrs geometry the deviations are significant (HF: 17%; DFT: 37%). The source of the discrepancies is clearly in the fact that the molecules are not pointlike.

In order to better assess this point, we have derived an expression for finite-length classical polarizable rods arranged in an infinite chain:

$$\alpha_\infty = \left[\frac{1}{\alpha(1)} - \frac{4}{b^3} \{ \zeta(3) + f^2 \zeta(5) + f^4 \zeta(7) + \dots \} \right]^{-1}, \quad (14)$$

where f is of the order of the ratio of the molecular length to the translation vector (i.e., 2 bohrs over 6 or 12 bohrs), and ζ 's are Riemann zeta functions.

In practice the magnitude of the terms after $\zeta(7)$ is negligible, while in the extreme Clausius–Mossotti-type case $f=0$. Overall, the “length” fb of the electron distribution of a molecule is not sharply defined. Nonetheless, using Eq. (14) with $f=2/12$ the error is reduced tenfold to 0.0002, while for the 6 bohrs case the improvement is much less impressive. While one could further fiddle with an optimum f value, we believe that Eq. (14) is enough to justify the general trend.

From a practical viewpoint, the extrapolated α_∞ values can be more accurately obtained from $\alpha(N) - \alpha(N-1)$ than from $\alpha(N)/N$, since at larger N 's the former is orders of magnitude closer to α_∞ than the latter. Even the numerical noise seen in the right lower panel of Fig. 4 for $N \geq 100$ cannot negate the fact that when the noise appears $\alpha(N) - \alpha(N-1)$ is already within 10^{-5} from the asymptotic α_∞ value.

B. Polyacetylene chains

The H_2 chains case dealt with so far concerned a chain of weakly interacting closed-shell units, whose interaction is tunable via the intermolecular separation. Now we switch in a sense to the opposite extreme. Polyacetylene chains $C_{2N}H_{2N+2}$ are covalently bonded conjugate systems and the interaction between the monomers is nontunable and strong. We have chosen the same geometry as in Fig. 1(b) of Ref. 9,

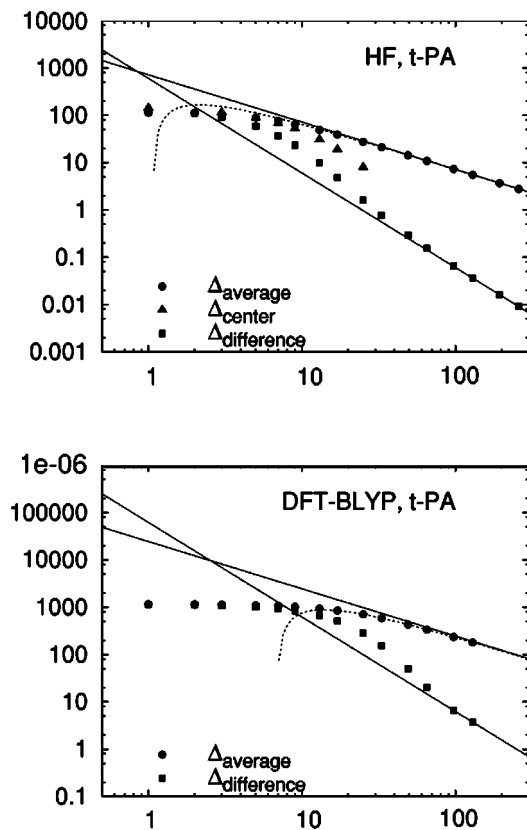


FIG. 5. First-principle longitudinal polarizabilities of transpolyacetylene chains within HF and DFT. $\Delta_{\text{average}} = \alpha_{\infty} - \alpha(N)/N$; $\Delta_{\text{center}} = \alpha_{\infty} - \alpha_{\text{center}}(N)$; $\Delta_{\text{difference}} = \alpha_{\infty} - \alpha(N) + \alpha(N-1)$. The slope of the straight solid lines in the logarithmic plots is -1 for Δ_{average} and -2 for $\Delta_{\text{difference}}$. In the former case the expansion to the next leading term beyond the first is used for the actual fit (dashed lines).

and performed HF calculations up to $N=257$ and DFT-BLYP up to $N=129$. Our results are all reported in Fig. 5 by means of log-log plots. Our calculated asymptotic values for α_{∞} are 166.76 (HF) and 1190 (DFT-BLYP), respectively. Obviously, for a covalently bonded conjugated system like polyacetylene it makes little sense comparing α_{∞} to $\alpha(1)$ by means of Eq. (7) since it is not really clear what $\alpha(1)$ is in this case.

We made an independent check of our fitted α_{∞} values by exploiting a recently developed finite-field code²⁷ for the periodic system. For good accuracy the higher order contaminations were removed from the numerical polarizabilities via a Romberg-type procedure as discussed in Ref. 9. In the HF case the two α_{∞} values agree to all meaningful significant digits (six) obtainable from the fit, while for DFT-BLYP the deviations are larger than the accuracy of the fit. We attribute this to numerical issues due to the exchange-correlation quadrature, combined with the fact that the DFT-BLYP polarizability turns out to be very large. We verified such conjecture by performing a similar comparison for H_2 chains (where the polarizability is smaller and the extrapolation is trivial): a similar trend occurs.

Even for polyacetylene, the log-log plots clearly indicate the universal asymptotic behavior emphasized throughout this work. The DFT polarizabilities are one order of magnitude larger than the HF ones, and much larger than the accurate results obtained in the literature from correlated wave

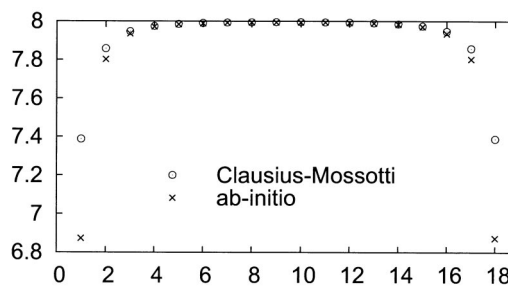


FIG. 6. Local polarizabilities per site $\alpha_i(N)$, for a stack of $N=18$ sites at $b=6$ bohrs separation. Crosses: values obtained from the Maestro–Moccia (Ref. 25) decomposition in the HF case. Circles: values obtained for the classical system, where we have used $\alpha(1)=6.7929$. By construction, the classical and the quantum system share the same asymptotic value $\alpha_{\infty}=8.0031$.

functions. We have already noted that such large values are a known pathology of the most common functionals within DFT.^{9–12} However, we stress once more that the qualitative asymptotic behavior found here in the limit of large- N oligomers is a consequence of quasi-one-dimensional electrostatics and does not depend on the approximations adopted to solve the quantum-mechanical problem.

The idea of fitting a generic oligomer property to a power series in $1/N$ is definitely not new: it has been proposed long ago²⁸ and implemented for the case of polarizability many times since then.^{1,3} However, these were “blind” fits, lacking a physical basis. As a matter of fact, alternative extrapolation schemes have been suggested and implemented over the years, including logarithmic^{4,29} or exponential^{2,5} forms and Padé approximants.^{7,30} These schemes have survived in the recent literature—in alternative to the $1/N$ -power series, with no conclusive assessment of the relative merits.⁸

To the best of our knowledge, the only paper where the size dependence of $\alpha(N)$ is investigated on the basis of a physical model in conjugate polymers is Ref. 15. In our notations Eq. (6) therein reads

$$\alpha(N) = \alpha_{\infty} \frac{N^2}{N + C}, \quad (15)$$

where C is a constant. We note that Eq. (15) has been derived from an extreme tight-binding Hamiltonian, using some further approximations. It is then remarkable that the single-parameter formula of Eq. (15) agrees with our Eq. (11) to leading order, although it disagrees to the following order, when e_1 and e_2 are taken from a fit to our first-principle calculations.

IV. LOCALIZED ORBITALS AND THE MODERN THEORY OF POLARIZATION

It is expedient to address a chain of moderate length, and to compare its Maestro–Moccia²⁵ local polarizabilities with their analog for the classical system. We plot the results for a stack of 18 H_2 molecules at $b=6$ bohrs separation in Fig. 6 (crosses). Therein, it is clearly seen that the $\alpha_i(N)$ values show qualitatively the same kind of convergence to their bulk value. In order to emphasize such similitude, the plot

for the classical model system (circles) refers to $\alpha(1) = 6.7929$, which reproduces, via Eq. (7), the first-principle asymptotic value. We are mapping in this way the H_2 chain onto a Clausius–Mossotti one, where the bulk polarizability is equal by construction. One should not expect an ideal match at all sites, though, given the finite extent of the H_2 electronic charge, the response in the end regions is actually different. Regardless, the comparison is useful to see the qualitative trend.

In this work we have solely addressed finite systems, whose wave function vanishes at infinity and is square integrable, using a typical quantum-chemistry framework. An alternative approach is possible in order to directly address the infinite- N limit. This approach is typical of solid-state physics and is based on periodic boundary conditions. At the HF or DFT levels the periodic boundary conditions lead—in the case of crystalline systems or stereoregular polymers—to canonical orbitals having the Bloch form. These can be transformed to localized Wannier orbitals, and the Boys criterion leads to the “optimally localized” Wannier orbitals as defined and computed by Marzari and Vanderbilt (MV).³¹ In fact, the MV orbitals are precisely the infinite-system analog of the Boys orbitals. For a chain of size N in the large- N limit, the Boys orbitals in the central region converge—basically by definition—to the corresponding MV orbitals of the infinite chain.

Within periodic boundary conditions the polarization problem is a very tough one, whose complete solution is only one decade old. This definitive solution is known as “the modern theory of polarization,” and has revolutionized the field, even as a matter of principle.^{32,33} We are not attempting to give here an overview of the modern theory. Suffice to say that, if canonical Bloch orbitals are used, the polarization takes the form of a Berry phase,^{34,35} nowadays implemented as a standard option in several codes for crystalline electronic-structure calculations.³⁶

A basic tenet of the modern theory states that the change in electronic macroscopic polarization induced by a given perturbation is exactly determined by the displacements of the centers of the Wannier orbitals. Therefore the Clausius–Mossotti model is “exact,” provided one interprets the local moments μ_i as Wannier-center displacements. Notice also that, while the local field is no longer a relevant quantity in the quantum case, yet the local polarizabilities defined in analogy to Eq. (3) remain valuable concepts.

The exact partitioning of the total polarization into localized contributions applies to any nonmetallic solid, including of course covalently bonded ones. This latter observation gives a clue why, even in polyacetylene, the mapping of the quantum system onto a Clausius–Mossotti classical model works heuristically so well. The key difference—common to both quasi-one-dimensional and three-dimensional systems—between the classical model and the quantum system is the spatial extent of the polarizable charge: pointlike in the former case, finite in the latter case (the size being governed by the spread of the localized orbitals).

What is not common to quasi-one-dimensional and three-dimensional systems is the penetration of end/surface effects into the bulk. In fact, it has been perspicuously shown

long ago that such penetration is short range in the former case,^{16,17} while the figures displayed in the present work emphasize the long-range penetration in the latter case.

V. DISCUSSION AND CONCLUSIONS

We have shown that the linear polarizability per unit cell of stereoregular oligomers of increasing size N converges to the asymptotic value by a universal power law, owing to electrostatic features. We stress that we are not addressing other intensive properties (such as the energy per cell), whose convergence properties might well be quite different.

On the basis of our findings, we are suggesting fitting formulas which exploit the finite- N calculations in several different ways, elucidating their mutual relationships. In contrast to all the previous work in the field (with the exception of Ref. 15), our suggested fitting form is based on physical concepts. In fact, our heuristic fitting to a simple Clausius–Mossotti-type classical model is inspired and strongly supported by the modern theory of polarization,³² which allows the exact mapping of the macroscopic polarization into localized—although not pointlike—dipoles, for any nonmetallic system.

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$$\sum_{k=1}^M \frac{1}{|k|^3} \frac{1}{|M+1-k|^2} \propto \int_1^M \frac{dk}{|k|^3 |M+1-k|^2} = O(1/M^2).$$

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