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Ground State Geometries of Polyacetylene Chains from Many-Particle Quantum Mechanics

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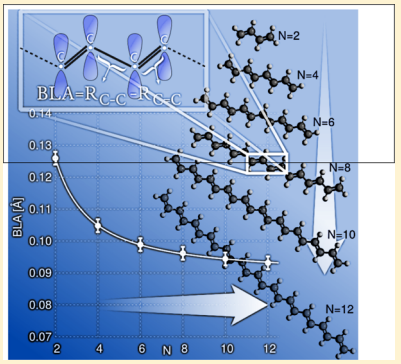
Supporting Information

ABSTRACT: Due to the crucial role played by electron correlation, the accurate determination of ground state geometries of π-conjugated molecules is still a challenge for many quantum chemistry methods. Because of the high parallelism of the algorithms and their explicit treatment of electron correlation effects, Quantum Monte Carlo calculations can offer an accurate and reliable description of the electronic states and of the geometries of such systems, competing with traditional quantum chemistry approaches. Here, we report the structural properties of polyacetylene chains H–$(C_2H_2)_N$–H up to N = 12 acetylene units, by means of Variational Monte Carlo (VMC) calculations based on the multi-determinant Jastrow Antisymmetrized Geminal Power (JAGP) wave function. This compact ansatz can provide for such systems an accurate description of the *dynamical electronic correlation* as recently detailed for the 1,3-butadiene molecule [J. Chem. Theory Comput. **2015** 11 (2), 508–517]. The calculated Bond Length Alternation (BLA), namely the difference between the single and double carbon bonds, extrapolates, for $N \rightarrow \infty$, to a value of 0.0910(7) Å, compatible with the experimental data. An accurate analysis was able to distinguish between the influence of the multi-determinantal AGP expansion and of the Jastrow factor on the geometrical properties of the fragments. Our size-extensive and self-interaction-free results provide new and accurate *ab initio* references for the structures of the ground state of polyenes.



INTRODUCTION

π-Conjugated organic molecules play an essential role in many physical, chemical, biological, and industrial fields, such as in polymer science, materials science, and biology. The unique electronic properties of organic conjugated polymers are for instance applied in light-emitting diodes, field-effect transistors, photovoltaic cells, and other optoelectronic devices.[1−3] In biology, long conjugated polymers are diffuse as light-absorbing chromophores for energy conversion, signaling, and photosynthesis. The π-conjugated scaffold of the majority of the biological pigments permits a fine-tuning of their properties through geometrical and field effects induced by the protein environment. The geometrical distortions influence their electronic and spectroscopic properties by changing the degree of conjugation along the molecule, measured as the difference in the lengths of adjacent single and double carbon bonds.[4]

The prototype for these π-electron conjugated molecules is *trans*-polyacetylene (PA), an organic polymer built from the repetition of N elementary acetylene C_2H_2 units, i.e., H–$(C_2H_2)_N$–H. In PA chains, which belong to the C_{2h} symmetry group, the degree of conjugation is measured through the difference in length of the single and double carbon bonds in the center of the chain, defined as the bond length alternation (BLA). This structural property strongly modulates the electronic properties of polyacetilene, such as polarizability and hyper polarizability,[5] and is predicted to be linearly dependent on the electronic gap between the valence and conduction bands.[2,4,6] As the number N of elementary C_2H_2 units grows, the BLA decreases to a constant value, which has been predicted to be around 0.08–0.09 Å by NMR[7] and X-ray.[8,9] The great interest of the scientific community for these oligomer chains is basically due to this small but not null BLA, which is the property that characterizes their nature of semiconductors. When doped, for example by arsenic pentafluoride (AsF_5),[10,11] charge defects appear, causing the BLA to locally vanish and leading to a nearly energy free conductivity of the charge defects along the polymer's longitudinal axes.

Despite their chemical simplicity, the quantum mechanical description of polyacetilene, even in the geometries in which the ground state is not degenerate, i.e., BLA equal to zero, requires high-level quantum chemistry calculations to correctly include both *dynamical* and *static* contributions to the correlation energy.[4] For this reason, the extrapolation of the structural properties of infinite PA chains and, in particular, of the BLA (BLA_∞), is still a difficult task for all the computational approaches used in quantum chemistry. In particular, Hartree–Fock (HF) and Møller–Plesset (MP) perturbation theory predict values of the BLA_∞ which are respectively too large, 0.122 Å,[12] and too small, 0.06 Å,[13−15] if compared to the

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experimental values (0.08−0.09 Å).[7−9] In Density Functional Theory (DFT), both the decay and the asymptotic value of the BLA as a function of N are strongly dependent on the choice of the exchange-correlation functional. The Self-Interaction Error[5,16,17] (SIE) leads to the delocalization of the charge distribution, usually underestimating the BLA_∞,[16,18] no matter if Local Density Approximation (LDA), Generalized Gradient Approximation (GGA), or hybrid functionals[19] are used, and predicting a value of the BLA_∞ usually between 0.03 and 0.06 Å.[18] Only the Half&Half hybrids like BHHLYP that use a larger percentage of HF exchange behave differently, reaching a value of 0.088 Å.[18] Another failure of DFT can be seen in the description of the longitudinal polarizability per elementary unit that tends to diverge as the chain grows.[5,20] To attenuate this erroneous behavior, empirical corrections have been introduced in the so-called Long Range Corrected (LC) functionals, that increase the percentage of HF exchange in the long-range interactions (CAM-B3LYP, LC-BLYP, ωPBEh, etc.).[5,20] These empiric corrections also affect the predicted values of the BLA_∞, which are larger than those given by traditional exchange-correlation functionals, between 0.09 and 0.10 Å.[14]

Up until now, the most accurate *ab initio* structural calculations, considered as references, are those obtained through the Coupled Cluster (CC) method with single, double, and triple perturbative excitations, i.e., CCSD(T),[21] which due to the computational cost are limited to chains of 12 carbon atoms (N = 6, $(C_2H_2)_N$ units).[21] These calculations use a rather small basis set (6-31G*) with the frozen core (FC) approximation and are unable to predict converged estimations of the carbon bond lengths.[21] Despite this, it was shown for the smallest conjugated PA chain, i.e., *trans*-1,3-butadiene, that the effect of the basis sets on the BLA[22] even though not negligible (the variations are in a range of 0.005 Å) is less than the effect of the order of the excitations considered in the CC ansatz. For *trans*-1,3-butadiene, the BLA predicted through CCSD is 0.01 Å longer than that obtained through CCSD(T), and this difference does not depend on the basis set.

Recently, Hu and Chan have published DMRG-CASSCF calculations[23] studying the relaxed PA structures of the ground state and of the first "dark" electronic excitation. In this work, the authors report the overestimation of the excitation energies and ascribed it to the missing of *dynamical correlation*.[23] Moreover, the structures of the ground states for chains of N = 6, 8, 10 elementary units, reported in the Supporting Information, present bond lengths that are similar to those of the CCSD(T) calculations, which are unconverged with respect to the basis sets, and values of the BLAs that seem to converge to 0.0886 Å already for chains of N = 8 elementary units.

Quantum Monte Carlo (QMC) methods[24] can provide a valid alternative to the standard quantum chemistry techniques for the accurate determination of the electronic properties and of the ground state geometries of long conjugated polymers such as PA chains of increasing size.

The reasons for the success of these techniques is due to the accurate quantum many-body description of the electronic correlation effects, coupled with the favorable scaling of the algorithms with respect to the number of the electrons, usually between the third or fourth power,[25] and with the possibility to use efficiently massively parallel computer resources. Using a compact and highly correlated multi-determinant variational wave function, the Jastrow Antisymetrized Geminal Power (JAGP) wave function,[26,27] it has been shown that for many cases the results obtained at the Variational Monte Carlo level are often indistinguishable in terms of relative energies by those obtained by higher-level Diffusion Monte Carlo approaches.[28,29] Examples of the applications of QMC methods to correlated molecules range from geometries and energetics of small compounds,[28−31] π-conjugated systems,[25,32−34] radicals and diradicals,[35,36] polarizabilities,[37] and *ab initio* molecular dynamics.[35,38−40] In the present work, we study the convergence of the structural properties of PA chains through VMC methods with the JAGP wave function. With a relatively small basis set we are able to give converged structural parameters, verified also at the Diffusion Monte Carlo (DMC) level,[41] and an extrapolated value of the BLA for infinite chains which is compatible with the experimental measurements.[7−9] We will also address the question of how *electronic correlation* affects the convergence of the degree of conjugation as the length of the PA chains grows, distinguishing between the contributions given by the various elements of our JAGP wave function.

Before discussing our results, in the following section, we will briefly describe the computational approach and the JAGP ansatz that is particularly suitable for describing conjugated systems.

COMPUTATIONAL APPROACH

Quantum Monte Carlo (QMC)[24] methods are stochastic variational procedures used to calculate the mean values of different physical observables on a given trial wave function that are now been applied for the study of various molecular compounds.[42,43] The great advantage of these techniques is that they can easily integrate complex parametrized wave functions that can also include explicit terms that couple the electronic variables with affordable computational costs. In addition, the stochastic QMC algorithms are very easy to parallelize, making them extremely suitable for the large high performance computing facilities with a large number of cores and small memory per core that will dominate the next generation of computer systems. As anticipated in the Introduction, the wave function used in our investigation is the Jastrow Antisymetrized Geminal Power (JAGP)[26] already applied by us to study different properties of various carbon compounds[28,29,37] and in particular the degree of conjugation of the *trans*-1,3-butadiene molecule.[41] This ansatz is the product of two terms: the Antisymetrized Geminal Power (AGP)[44] wave function that is based on the Resonating Valence Bond (RVB) representation introduced by Pauling to describe the chemical bonds[45] and a Jastrow factor[28] that is similar to the Gutzwiller ansatz already used to study correlation effects in PA chains.[46,47]

For PA chains, whose ground state is in a spin singlet state, the AGP is written as an antisymmetrized product of $N_e/2$ geminal wave functions, being N_e the number of electrons in the system. Each geminal wave function is a spin singlet state, written as the linear combination of products of two atomic orbitals

$$\phi_G(\mathbf{x}_i, \mathbf{x}_j) = \sum_{a,b} \sum_{\mu,\nu} \lambda_{\mu_a,\nu_b} \psi_{\mu_a}(\mathbf{r}_i) \psi_{\nu_b}(\mathbf{r}_j) \frac{1}{\sqrt{2}} [|\uparrow\rangle_i |\downarrow\rangle_j - |\downarrow\rangle_i |\uparrow\rangle_j] \quad (1)$$

where the λ_{μ_a,ν_b} coefficients can be implemented as coupling valence bonding constants between the μ and ν orbitals centered on the a-th and b-th atoms. For example, the λ_{μ_a,ν_b} coefficients associated with the p_z atomic orbitals, orthogonal to the molecular plane, modulate the π coupling in the PA

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chains.[41] This ansatz is a multi-determinantal expansion, that includes a constraint set of molecular excitations.[41,48,49] This can be seen by diagonalizing the Geminal expansion (eq 1), projecting it on a set of orthogonalized molecular orbitals built as the linear combination of the primitive orbitals that appear in eq 1:

$$\varphi_k(\mathbf{r}) = \sum_{a=1}^{M} \sum_{\mu} c_{\mu_a}^k \psi_{\mu_a}(\mathbf{r}) \tag{2}$$

In this way, the geminal expansion becomes a sum over doubly occupied n molecular orbitals:

$$\Phi_G^{mol}(\mathbf{x}_i; \mathbf{x}_j) = \sum_{k=1}^{n} \tilde{\lambda}_{kk} \varphi_k(\mathbf{r}_i)\varphi_k(\mathbf{r}_j) \frac{1}{\sqrt{2}} [|\uparrow\rangle_i|\downarrow\rangle_j - |\downarrow\rangle_i|\uparrow\rangle_j] \tag{3}$$

and the projection from eq 1 to eq 3 becomes an exact mapping when n is equal to the number of atomic orbitals in the basis set. In the expansion of eq 3, the ratio $\tilde{\lambda}_{\mathrm{LUMO}+k}/\tilde{\lambda}_{\mathrm{HOMO}}$ between the coefficients associated with the HOMO and LUMO+k molecular orbitals are a measure of the weight of the excited configurations in which the double occupied HOMO orbital is substituted by the doubly occupied LUMO+k. Obviously, when $n = N_e/2$, the molecular JAGP expansion reduces to a single Slater determinant with the Jastrow factor (JSD). Because of the Jastrow factor and because of the possible rotations in the Hilbert space, the molecular orbitals $\varphi_k(\mathbf{r})$ that come from the projection of the JAGP cannot be equal to those obtained through single particle approaches. Still, by studying the modulation of the $\tilde{\lambda}$ in the expansion, it can be possible to extract informations able to help the characterization of the chemical electronic state of the molecule, as done, for example, for the diradical species in refs 36 and 48. The particularity of the JAGP ansatz is that it contains in its variational space three chemical states of the PA chains[41] summarized in Figure 1: the

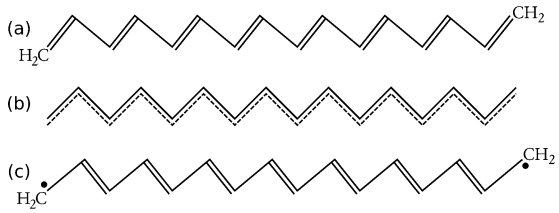

Figure 1. Electronic chemical states included in the AGP ansatz and separated by different structural minima: (a) ground state configuration, (b) resonating electronic configuration with identical carbon bonds, and (c) inversion of the single and double bonds, diradical state, with two localized electrons on the ending CH_2 groups.

highly dimerized ground state, which is typical of the HF solution; the resonating electronic state[50] in the limit of null BLA and characteristic of the metallic phase for infinite chains; and the diradical state,[48] which inverts the single and double carbon bonds in finite chains, localizing two unpaired electrons on each CH_2 ending group. As discussed in ref 41, the presence of these possible chemical states guarantees that the JAGP is able to contain all the *static correlation* necessary for the description of the π conjugation on PA chains, and in particular, it is able to connect the state with finite BLA (observed experimentally) to that of zero BLA in the limit of conductive chains, with degenerate HOMO and LUMO orbitals. Even though it was demonstrated in ref 41 that the dominant contribution to the description of the conjugation of *trans*-1,3-butadiene is due to the *dynamical electronic correlation*, it is still unclear how the inclusion of higher order molecular orbitals in the multi-determinantal expansion contributes to the description of the conjugation for larger PA chains in which the BLA gradually decreases.

Recently, through DMRG-CASSCF calculations, Hu and Chan[23] have confirmed that the dominant contribution for the description of the ground state of PA chains comes from *dynamical electronic correlation*, being that the ground state is essentially a single determinant.

In order to distinguish the effects on the degree of conjugation of both the Jastrow factor and the multi-determinantal contribution, we have compared the results obtained with the JAGP and the JSD anästze.

The QMC calculations have been done with the TurboRVB[51] package from Sorella and co-workers. The wave function has been optimized with the linear method with Hessian acceleration described in ref 52, improved through the reweighting technique described in ref 35. The structural optimization has been done through the method described in ref 28 using the scheme described in ref 53. Following the procedure established in previous works, the core electrons of the carbon atoms are substituted by Energy-Consistent Pseudopotentials (ECP).[54] For the JAGP structural optimizations, we have used a basis set build of (4s4p)/[2s2p] contracted Gaussian orbitals for the carbon atoms, and of (3s3p)/[1s1p] contracted Gaussian orbitals for the hydrogen atoms. The JSD calculations are done with an uncontracted basis set of (5s5p2d) Gaussian primitives for the carbon atoms and of (3s2p) Gaussian primitives for the hydrogen ones. The basis set used for the three body Jastrow factor is built of (4s3p)/[2s2p] contracted orbitals for the carbon atoms and of (3s2p)/[1s1p] contracted Gaussian orbitals for the hydrogen atoms. In order to calculate the polarizability, we have used the finite difference method,[37] with an external electric field of 0.001 au. For these calculations, we have used the JAGP ansatz with a larger basis set of contracted Gaussians with (5s5p2d)/[3s2p1d] orbitals for the carbon atoms and of (4s3p)/[2s1p] orbitals for the hydrogen atoms and using the same Jastrow factor described above.

The quantum chemistry calculations have been done with the NWchem 6.1.1[55] package.

RESULTS AND DISCUSSION

Bond Lengths and local Bond Length Alternation. For PA chains of finite length, the effect of the CH_2 ending groups spreads along the chain towards the center, affecting the local degree of conjugation and the length of the various carbon bonds.

The bond lengths of our molecular systems, obtained with different computational methods, are all shown in Figure 2, where because of the C_{2h} symmetry only half the chains are reported, starting from the central C_1-C_2 single carbon bond.

In this figure, the *ab initio* HF, MP2, and the CC calculations from ref 21 are all obtained with the 6-31G* basis set and are displayed in the lower panel together with the DMRG results from ref 23 (M = 1000) and our JSD and JAGP calculations. The DFT calculations are shown in the top panel and are obtained with the B3LYP, CAM-B3LYP, and ωPBEh exchange-correlation functionals using the larger cc-pVTZ basis set.

Already examining the length of the carbon bonds, it is possible to classify how the different approaches describe the π

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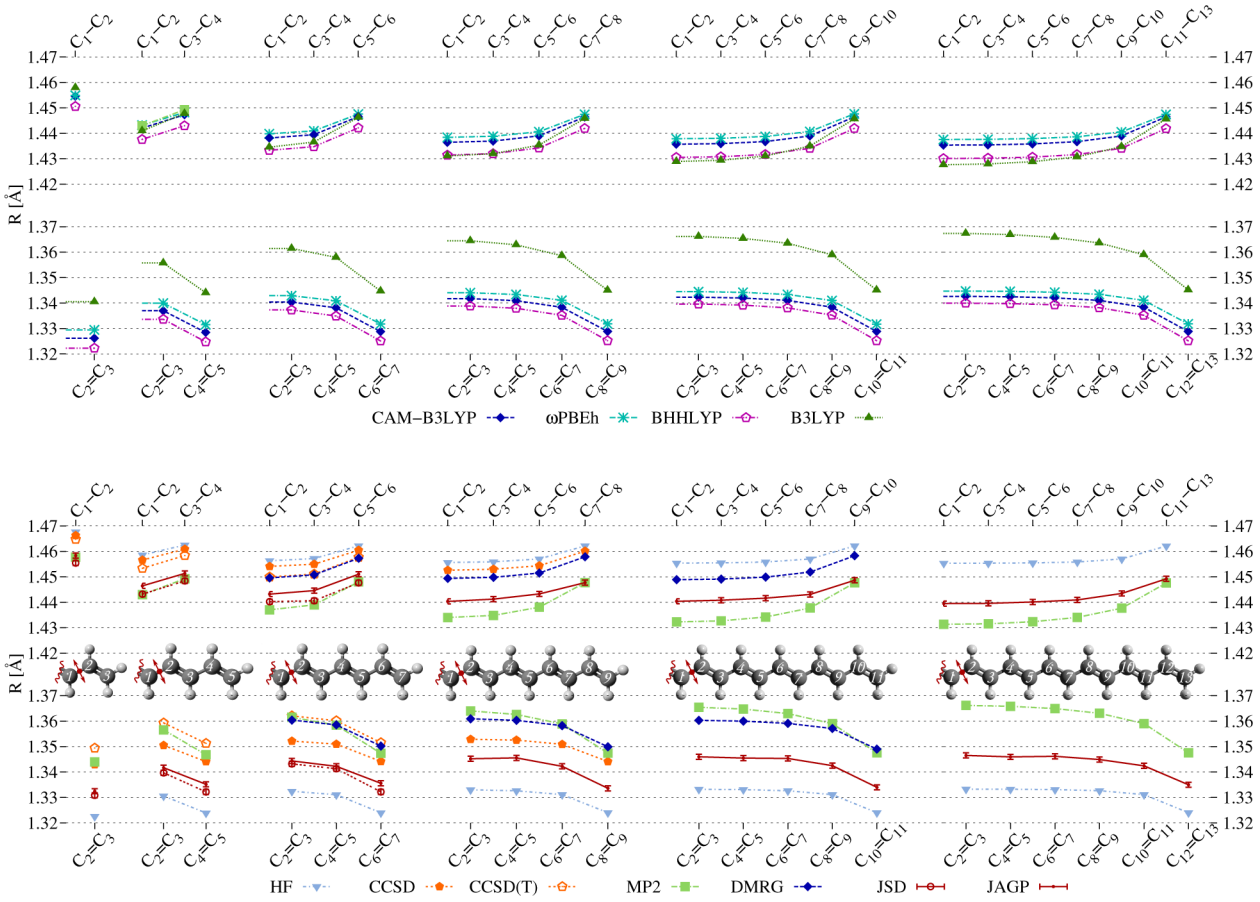

Figure 2. Carbon bonds for polyacetylene chains of different lengths $N = \{2, 4, 6, 8, 10, 12\}$ calculated with different methods, and reported as a function of the distance from the center of the chain. The *ab initio* HF, MP2, and the CC calculations from ref 21 are all obtained with the 6-31G* basis set, while the DFT calculations with the B3LYP, CAM-B3LYP, and ωPBEh exchange-correlation functionals have been computed using the larger cc-pVTZ basis set. The DMRG results are those reported in the Supporting Information of ref 23 obtained with $M = 1000$. The top figure displays the results obtained from DFT with different functionals, while the bottom figure displays the results from *ab initio* methods.

conjugation. The HF results represent the case of high charge localization of the double bonds, which are shorter then those predicted by the other methods, whereas at the same time single bonds are longer. At the opposite, MP2 and B3LYP calculations tend to delocalize the charge, shortening the single bonds and elongating the double ones. The increase in the HF exchange in the BHHLYP functional leaves the single bonds unchanged with respect to the B3LYP functional, and the major effect can be found in the contraction of the double bonds that are much similar to those obtained by HF. In particular, the BHHLYP double bonds linked to the CH_2 ending groups have the same lengths as in HF calculations. Differently, the two long-range corrected exchange-correlation functionals, CAM-B3LYP and ωPBEh, give intermediate results between the highly localized HF case, and the highly delocalized B3LYP and MP2. In particular, the long-range correction affects the elongation of the double bond, which is more then halved with respect to the case of B3LYP and MP2. The absolute bond lengths of the CC results, as discussed in refs 22 and 41, are not reliable because of the incompleteness of the basis set. Whereas the double bonds elongate, the single bonds remain similar to those given by HF calculations.

Examining the DMRG results from ref 23, we can see that they essentially correspond to the CCSD(T) geometries which are unconverged with respect to the basis set.

Using Variational Monte Carlo, we have carried out the structural optimizations of PA chains with $N = \{2, 4, 6, 8, 10, 12\}$ elementary units using the JAGP ansatz. In order to understand the effects of the multi-determinantal expansion and of the Jastrow factor on the local structural parameters, we also compare the JAGP results with those obtained with the single-determinant JSD wave function on PA chains of $N = \{2, 4, 6\}$ elementary units. A first comparison between the JAGP and the JSD bond lengths confirms the results obtained in previous investigations on smaller molecules;[28,29,41] the difference is rather small, with the JAGP elongating both the bonds of about 0.002 Å. As described in our previous work on butadiene,[41] this was ascribed to the *dynamical correlation* of the AGP expansion, recovered by those configurations that include the antibonding LUMO and LUMO+1 orbitals that change the nodal surface of the wave function. The single bond is the most affected by the use of the multi-determinantal wave function, and by examining accurately Figure 2, it can be seen that the JAGP tends to elongate all the bonds in a uniform way. On the other hand, comparing the results for the $N = \{4, 6\}$ chains, we can see that the elongation of the double bonds is not uniform and that the JAGP elongates more the double bonds linked to the CH_2 ending groups.

We also note that our VMC calculations give structural parameters that are quite similar to those obtained with the two long-range corrected functionals; in particular, the JSD and

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ωPBEh structural parameters for the N = {2, 4, 6} chains are within the error bars. We will further comment this agreement in the following sections.

To enlighten the effects of the ending groups on the local conjugation, in Figure 3, we compare the local BLA, defined as

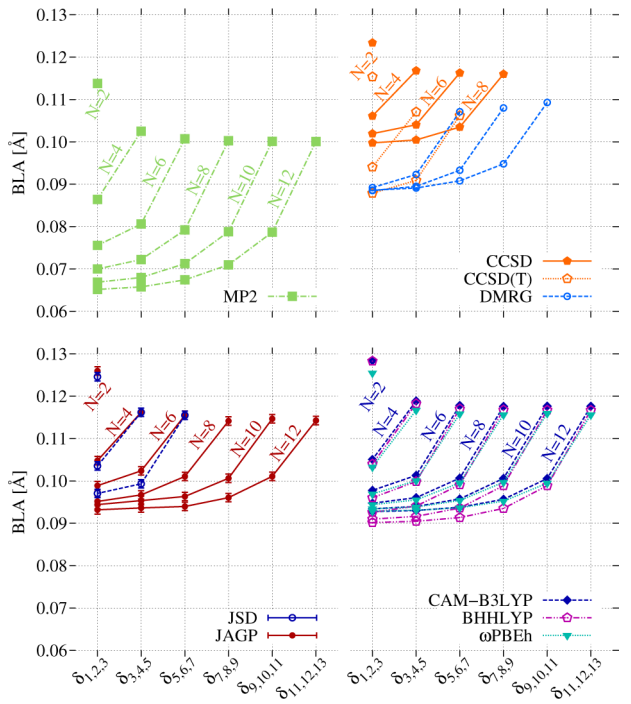

Figure 3. Local BLA for different chain lengths obtained from the bonds reported in Figure 2.

the difference between adjacent single and double bonds $\delta_{i-1,i,i+1} = R_{C_{i-1}-C_i} - R_{C_i = C_{i+1}}$ of the chain for VMC, DMRG, MP2, CCSD, and CCSD(T) and for the DFT functionals BHHLYP, CAM-B3LYP, and ωPBEh. As expected, this quantity usually decreases from the end towards the center of the chain, and the effect of the ending CH_2 groups spreads along the chain for at least five elementary units, or even more if we consider the MP2 results.[14]

An anomalous behavior can be recognized in Figure 3 for the DMRG calculations.[23] In disagreement with the other predictions, the BLA near the ending groups grows with the size of the chain instead of decreasing and that in the center remains nearly constant. As the authors point out, the ground state of the *trans*-PA chains is essentially a single determinant,[23] and the *dynamical correlation* is the fundamental ingredient for the correct description of the equilibrium structures. The fact that the DMRG bonds in Figure 2 are similar to the unconverged CCSD(T) predictions and that the local BLA in Figure 3 manifests an unexpected behavior might be therefore related to a non uniform recovery of the *dynamical correlation* for the chains of different length. This hypothesis is also confirmed by the authors that ascribe to this same defect also their overestimation of the excitation energies.[23]

The local BLA predicted through CCSD(T) is nearly 0.01 Å lower than that obtained by CCSD, but the effect is not uniform along the chain. Surprisingly, the BLA of *trans*-1,3-butadiene is identical for CCSD(T) and for the highly delocalized results given by B3LYP or MP2.

Again the long-range corrected functionals give an intermediate result between the highly delocalized calculations and that predicted by HF. The BHHLYP results are similar to those obtained through the CAM-B3LYP and ωPBEh functionals, but still it is evident that it tends to spread the charge localization further then the two long-range corrected functionals. CAM-B3LYP and ωPBEh are similar to the results given by our *ab initio* quantum Monte Carlo results with both the JAGP and JSD ansätze. Between the JAGP and JSD wave functions, some particular differences appear. The BLA of the ending groups for N = {4, 6} is identical for the two wave functions, whereas towards the center of the chain it changes, likely because of the effect of the antibonding orbitals which is not uniform on the single and double bonds.

Central Bond Length Alternation and Its Convergence Behavior. To study the conjugation in the limit of infinite chains, the first step is to define the correct function able to describe the asymptotic behavior of the central BLA of the chain as a function of the number N of elementary acetilene units. In the literature, many different functions have been proposed, based essentially on the exponential function and on polynomial series of $1/N$,[14] which all seem to fail in the proper description of the infinite limit.

After having considered different functional forms, we found that the best extrapolating function is a linear combination of Kuhn's fit,[2] at first used in ref 22, plus an exponential function:

$$f(N) = A\sqrt{1 + 2B\cos\left(\frac{\pi}{1+N}\right)} + Ce^{-DN} \quad (4)$$

This four parameters function, based on the linear dependency of the optical band gaps on the BLA,[2,22] was first proposed in ref 2 to study the optical band gaps of conjugated molecules, seeing that Kuhn's formula[56,57] was unable to take into account the charge transfer effects that can appear in the longest chains. Through the exponential decay, Kuhn's fit, and the four parameters function, we have revisited different results present in the literature summarizing them in Table 1S of the Supporting Information. We have verified that for the different quantum chemistry calculations (Figure 1S of the Supporting Information) the extrapolation given by Kuhn's fit predicts a lower bound to the value of the BLA and is unable to describe the exponential decay that dominates the converge for longer chains. The exponential decay alone, on the other hand, predicts a value for the BLA_∞ that is usually too large, representing an upper bound, and is inefficient in describing the convergence for smaller PA chains. Using this function, we have therefore extrapolated our JAGP results, together with those obtained with the CCSD and CCSD(T) calculations[14] (see data in Figure 2S of the Supporting Information).

Figure 4 reports the convergence of the central BLA of the PA chains as a function of the number N of elementary units, together with the values of the extrapolated BLA_∞ and the experimental predictions.[7−9]

The extrapolated BLA value from our JAGP calculations is around 0.0910(7) Å, compatible with that reported by experimental data on infinite PA 0.08−0.09 Å.[7−9] Interestingly, the same value is obtained from the long-range corrected DFT hybrid functionals CAM-B3LYP and ωPBEh. For CCSD, the extrapolated value was equal to 0.097 Å, while for CCSD(T) it was equal to 0.083 Å. The DMRG calculations from ref 23 display a rather unexpected behavior, as the BLA seems to converge extremely rapidly already for N = 6 and presents a

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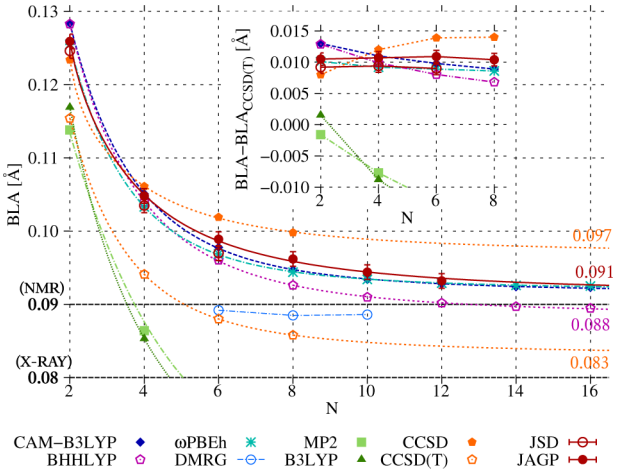

Figure 4. BLA as a function of the number of elementary units in the polyacetylene chain. In the inset panel, the differences of the BLA of the different methods with that of CCSD(T) for $N \in \{2, 4, 6, 8\}$. The *ab initio* MP2 and the CC calculations from ref 21 are all obtained with the 6-31G* basis set, while the DFT calculations with the B3LYP, CAM-B3LYP, and ωPBEh exchange-correlation functionals have been computed using the larger CC-PVTZ basis set. The DMRG results are those reported in the Supporting Information of ref 23 obtained with M = 1000. The dashed black lines indicate the NMR[7] and X-ray[8,9] experimental values.

rather flat slope that contradicts all other calculations. Together with what was found for the local BLA, this seems to confirm the missing or nonuniform recovery of the *dynamical correlation* that affects the structural description of the chains with this method.

In order to magnify the differences in the slopes of the convergences obtained from the various methods against the CCSD(T) reference, in the inset of Figure 4, we have reported the differences between the CCSD(T) BLAs and those obtained with all the other quantum chemistry calculations.

The interesting result that appears is that both the JSD and JAGP values are parallel to the CCSD(T) curve with a constant shift of 0.01 Å and that between the JAGP and JSD predictions there is only a small constant shift of about 0.002 Å. This result indicates that in Variational Monte Carlo the slope of the convergence of the BLA as a function of the number N of elementary units depends on the *dynamical correlation* described by the Jastrow factor. The difference of 0.01 Å between the BLAs obtained with CCSD(T) and JAGP was already discussed by us in ref 41. In this previous work, we showed that the Configuration Interaction (CI) calculations, with the increase in the order of excitations considered, seem to converge to the value of the BLA predicted by us through quantum Monte Carlo. Differently, CCSD(T) results were at variance with this convergence and displayed a BLA which was 0.01 Å smaller and similar for *trans*-1,3-butadiene to that predicted by the MP2 and B3LYP calculations that delocalize the charge. Through Lattice Regularized Diffusion Monte Carlo (LRDMC) calculations that recovers more *electronic correlation* even respect to CCSD(T), we showed that an optimized JAGP wave function and its nodal surface prefer the structural minima obtained from VMC JAGP optimizations with respect to that given by CCSD(T)/CBS extrapolation of about 0.030(11) eV.[41] Even though this result strongly suggests that the QMC structures are more accurate then those given by CCSD(T)/CBS calculations, it is not a definite test, as one should explore also the nodal surface of the CCSD(T) calculations which is not possible. In conclusion, one hypothesis for the discrepancy between the BLA predicted by CC and that given by CI and by quantum Monte Carlo was that as CC includes the excited configurations in a nonlinear way this may lead to a nonmonotonic convergence of the structural properties for conjugated systems.

JAGP and JSD Ansätze: Role of Multi-Determinantal Expansion. The QMC results show that the multi-determinant expansion of the AGP is only responsible for a small shift of the BLA of about 0.002 Å with respect to a single determinant JSD wave function (Figure 4). In addition, this small shift in the BLA, as shown in Figure 3, does not affect the BLA near the ending CH_2 units of the chains but only the most internal bonds. To rationalize these issues, we used the diagonalized AGP in the space of the molecular orbitals, defined in eq 3. To estimate the weight of the leading single Slater determinant configuration of the AGP, we have projected the JAGP wave function on a single determinant wave function with the same Jastrow factor (JSD). Please notice that these results are different from the JSD calculations presented in Figures 2, 3, and 4, as in the present case only a projection of an optimized JAGP on the JSD subspace is performed without further orbitals or Jastrow optimization. Through the correlated sampling VMC technique,[58] we have therefore calculated the overlap between the JAGP and JSD ansätze as well as the energy differences between the two wave functions on the JAGP equilibrium structure.

In Figure 5, we show the energy differences of the two wave functions per elementary unit $\Delta E/N = (E_{JSD} - E_{JAGP})/N$ as a function of N and the wave functions' overlaps.

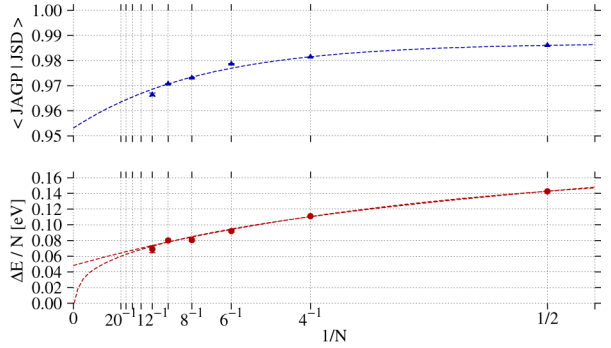

Figure 5. In the bottom panel, we show the difference between the energies per unit of the JAGP wave function and its projection over a single determinant JSD wave function, $\Delta E/N = (E_{JSD} - E_{JAGP})/N$. In the top panel, we show the overlaps between the JAGP and JSD wave functions as a function of the inverse of the number of elementary units N.

It is evident that as the chain length increases the overlap between the two ansätze gradually diminishes to a value around 0.95. This first result confirms that the effect of the multi-determinantal expansion is very small in the description of the ground state of the PA chains. As the chain grows, the value of the energy difference for elementary unit $\Delta E/N$ if extrapolated to the thermodynamic limit with the function $A + (C/N)^B$ goes to zero, while using the function $A(1 + Be^{-Cx})$, it goes to a constant value. It is probable, due to the insulating nature of the PA chains, that the difference goes to zero very slowly as according to the former trend, but in order to confirm this, it would be essential to study conformers of at least N = 30

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elementary units. Another more clear approach would be the use of periodic boundary conditions to study directly the infinite chains extrapolating for larger elementary units, as done for example in the study of graphene sheets by Marchi et al. in ref 50.

To answer the question about the origin of this multideterminantal contribution, we can project the JAGP on its diagonalized molecular representation (eq 3) with a number n equal to the dimension of the atomic basis set, so that the projection becomes an exact mapping. In Figure 6a, we report

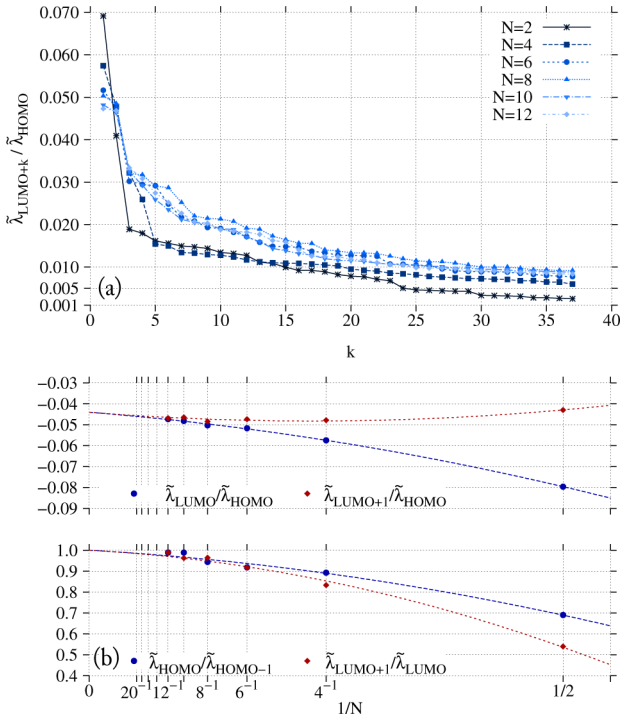

Figure 6. (a) Ratio between the $\tilde{\lambda}_{HOMO}$ and $\tilde{\lambda}_{LUMO+k}$ coefficients as a function of the chains' size. (b) Ratio between the $\tilde{\lambda}$ coefficients of the frontier HOMO−1, HOMO, LUMO, and LUMO+1 orbitals that characterize the molecular AGP expansion defined in eq 3.

the convergence of the weights of the $\tilde{\lambda}_{LUMO+k}$ coefficients over the $\tilde{\lambda}_{HOMO}$ one. By comparing the values of the $\tilde{\lambda}$ coefficients as done in refs 36, 48, and 50 with that associated with the HOMO orbital, it is possible to understand how the higher order configurations contribute to the AGP expansion in addition to the dominant SD component. In this case, as the chain grows, the weights of the higher molecular orbitals gradually increase, converging not all in a monotonic way. It must be remembered that the values of these weights are also affected by the Jastrow factor, as reported in ref 41, which also affects the amplitudes and the form of the molecular orbitals. One interesting aspect is that as the chain length increases both the $\tilde{\lambda}_{HOMO}/\tilde{\lambda}_{HOMO-1}$ and $\tilde{\lambda}_{LUMO+1}/\tilde{\lambda}_{LUMO}$ ratios converge to one, as shown in the lower panel of Figure 6b.

On the other hand, the weights of the $\tilde{\lambda}_{LUMO+1}$ and $\tilde{\lambda}_{LUMO}$ coefficients with respect to the $\tilde{\lambda}_{HOMO}$ one, shown in the top panel of Figure 6b, converge to a small constant value as the chain grows.

This small constant value is related to the fact that the configurations above the SD weight less than 5% in the multideterminantal AGP expansion for the electronic ground state of the PA chains, as expected from the chemical nature of these insulating systems.

The degeneracy between the weights of the $\tilde{\lambda}_{HOMO}$ and $\tilde{\lambda}_{HOMO-1}$ orbitals and between the $\tilde{\lambda}_{LUMO+1}$ and $\tilde{\lambda}_{LUMO}$ ones is predicting a component similar to the excited $2A_g$ state that has the same symmetry of the ground state.

As shown in the works by Hudson and Kohler,[59] the first low laying electronic excitation in polyenes is a $2A_g$ state that is a combination of three different electronic configurations, nearly degenerate, that describe respectively the promotion of the two HOMO electrons to the LUMO orbital, the promotion of an electron from the HOMO orbital to the LUMO+1 one, and the promotion of an electron from the HOMO−1 orbital to the LUMO one.[60]

A part from the leading SD, in the AGP, the small multideterminantal contribution is actually a reweighted combination of these three degenerate configurations that maintain the A_g symmetry of the ground state, and this explains the degeneracy in the weights shown in the lower panel of Figure 6. The two degenerate single excitations have all a relative weight with respect to the SD equal to $\sqrt{\frac{\tilde{\lambda}_{LUMO}}{\tilde{\lambda}_{HOMO}}} \approx 0.2$, while the double excitations involving the promotion of electronic couples from the HOMO and HOMO−1 orbitals to the LUMO and LUMO+1 orbitals weight $\frac{\tilde{\lambda}_{LUMO}}{\tilde{\lambda}_{HOMO}} \approx 0.04$. It is important to keep in mind that this latter weight is also associated with the singlet determinants in which all the four frontier orbitals are occupied by one electron. Thus, the excited contribution, introduced by the Fermionic part of the AGP, correcting the nodal surface, does not correspond exactly to the $2A_g$ state of PA, but it is a recombination of the important configurations characterizing this first excited state, and has the only effect of better recovering the *dynamical electronic correlation* necessary for the ground state.

Longitudinal Polarizability Per Elementary Unit. The longitudinal electronic polarizability α_{zz} is an important property that characterizes the electronic response of the PA chains to an external field and has been largely studied in the previous years.[20,61−67] In particular, in the study of this property the failures of traditional DFT functionals appeared, exposing their limitations and stimulating the development of the so-called long-range corrected functionals like CAM-B3LYP and ωPBEh. While the polarizability for elementary unit α_{zz}/N of the PA chains tends to converge toward a constant value as the chain grows, in DFT, the polarizability diverges in the worst case linearly.[20,64]

Having investigated the possibility to obtain accurate molecular structures with VMC with the JAGP and JSD ansätze, a last aspect must be explored in order to validate our description of the electronic ground state.

Following the finite difference approach already applied by us in ref 37, here, we calculate the longitudinal polarizability α_{zz} using the molecular structures obtained through VMC calculations on the JAGP ansatz (see Computational Approach section). The results are reported in Figure 7 and compared with the polarizabilities obtained with other quantum chemistry calculations present in the literature, each obtained on the ground state structural minima predicted by the method.

The introduction of *dynamical correlation* in *ab initio* approaches has the effect of lowering the polarizability per unit with repect to HF, as shown for MP2 or CCSD calculations.[20,64,66] This effect can be ascribed to both the

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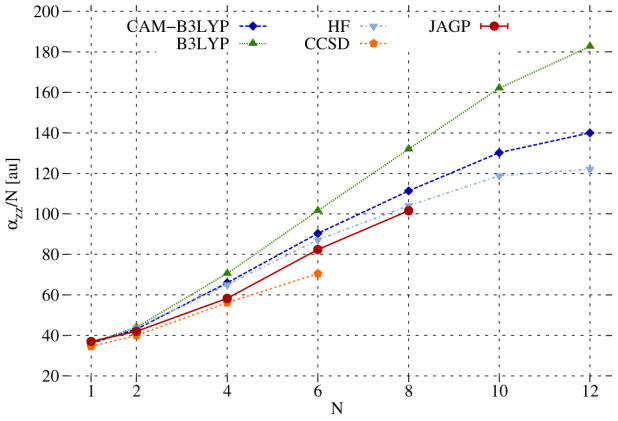

Figure 7. Electronic polarizability per C_2H_2 unit as a function of the number of units N. The other quantum chemistry calculations a part from those obtained with the JAGP are reported in ref 20.

finite basis set and the different structural equilibriums. Interestingly, while MP2 tends to delocalize the charge when looking at the bonds (Figure 2) or at the BLAs (Figures 3 and 4), for the polarizability, it acts similarly to the correlated CCSD method and at variance with respect to the B3LYP functional that gave similar structural results.

On the other hand, our JAGP α_{zz}/N results are again consistent with the previous calculated molecular geometries, giving an higher value for the polarizability respect to MP2 and CCSD.

CONCLUSIONS

Due to the electron correlation effects, the accurate determination of ground state geometries of long π-conjugated organic molecules is a fundamental albeit challenging task for various computational methods used in quantum chemistry. The structure tunes both the ground and excited state properties of conjugated biomolecules and polymers, but their estimations are strongly dependent on the computational approximation used. Each method displays limitations or errors, which are intrinsic to its nature, like the Self-Interaction Error in DFT or the charge delocalization of Møller–Plesset perturbation theory at the second order or the finite basis set errors of the feasible Coupled Cluster calculations. In this work, we have presented new *ab initio* references for the structures and the electronic properties of large polyacetylene chains, based on many-body Variational Monte Carlo calculations on a Jastrow Antisymmetrized Geminal Power (JAGP) ansatz. The QMC methods are free from the errors usually encountered in DFT or in perturbation theories, and because of the compactness of the wave function ansatz and the favorable scaling of these algorithms with the system size, they can fully exploit the correlated many-body wave function with a relatively small basis set.

Our structural optimizations give a BLA_∞ of 0.0910(7) Å, which is in agreement with the experimental values the lie around 0.08 and 0.09 Å.[7−9]

Through the comparison between the multi-determinantal JAGP and a Jastrow single determinant wave function (JSD), we have been able to enlighten the role played by the Jastrow factor and by the higher order configurations that appear in the multi-determinantal expansion. The *dynamical correlation* recovered by the Jastrow factor, a bosonic term that does not change the nodes of the wave function, appears to be the principal ingredient responsible for the correlation effects and the change of structure with respect to the uncorrelated HF calculations. Moreover it affects the "slope" of the convergence of the Bond Length Alternation (BLA) as a function of the number N of polyacetylene units. As a matter of fact, for both the JSD and JAGP ansätze, this "slope" is the same as the one obtained for the CCSD(T) calculations, while the values for each chain length are larger by a constant value of 0.01 Å, as already discussed by us in a previous work in the case of butadiene.[41] On the other hand, the inclusion of higher order configurations in the multi-determinantal AGP expansion only introduce a small contribution in the electronic correlation that affects only the local BLA near the center of the chains.

Even in the study of the electronic properties like the longitudinal polarizability per elementary unit α_{zz}/N, our VMC calculations display converged results with a better recovery of the *dynamical electronic correlation*. In addition, these overall accurate and consistent results represent a new *ab initio* reference for the evaluation of the different computational methods used in quantum chemistry for the study of the π-conjugated polymers and conjugated molecules.

In conclusion, in this work, we have addressed with unprecedented accuracy the structural and electronic properties of long polyacetylene fragments, prototypes of π-conjugated polymers. Our results demonstrate how quantum Monte Carlo methods have become an important and mature tool to characterize the structures and the electronic properties of large correlated systems. The possibility to deal with large compounds with fully many-body wave functions is overcoming the limitations and the intrinsic errors of other quantum chemistry methods, leading in the near future to enlighten with a purely *ab initio* approach the energetics and geometries of large π-conjugated molecules relevant for biology and material science.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00427.

In Table 1S, we recollect the various central BLAs as a function of the N elementary units present in the literature and obtained with various methods. The values have been extrapolated with the fits described in the article. Figures 1S and 2S show, respectively, the extrapolations of the HF, MP2, and CAM-B3LYP BLAs and the extrapolations of the data from the CCSD, CCSD(T), and JAGP calculations. (PDF)

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Notes

The authors declare no competing financial interest.

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