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Electron-correlation effects on the static longitudinal polarizability of polymeric chains. II. Bond-length-alternation effects

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Ab initio calculations of the static longitudinal polarizability of different molecular hydrogen model chains have been carried out at different levels of approximation to investigate the effects of including electron correlation as well as the variation of these effects as a function of the bond-length alternation of the systems. First, the coupled and uncoupled Hartree-Fock schemes have been employed. To assess the electron-correlation effects, the size-consistent Møller-Plesset treatments limited to second (MP2), third (MP3), and fourth (MP4) order in electron-electron interactions, as well as the coupled-cluster techniques including all double substitutions (CCD), all single and double substitutions (CCSD), and all single and double substitutions with a perturbational estimate of the connected triple excitations [CCSD(T)] have been used. Within the MP4 treatment, a decomposition of the electron-correlation corrections according to the different classes of substitutions and different order highlights the relatively greater importance of the double substitutions at second and third orders. The main findings are that (i) the coupled Hartree-Fock (CHF) technique overestimates the asymptotic static longitudinal polarizability per unit cell for the three types of H_2 chains under investigation; (ii) larger basis sets have to be employed when including electron correlation effects, otherwise, the correction is overestimated; (iii) these basis-set effects on the electron-correlation correction are enhanced in the case of the less alternating chains; (iv) using a sufficiently large atomic basis set, at the Møller-Plesset or CCSD(T) levels, the more conjugated the chains, the less the relative magnitude of the electron-correlation correction to the CHF value, whereas using the CCD and CCSD techniques, these relative electron-correlation corrections slightly increase in the case of the less alternating molecular hydrogen chains; and (v) the more conjugated the systems, the higher order the treatments of electron correlation required to get suitable values but the smaller the magnitude of electron-correlation correction.

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I. INTRODUCTION

The evaluation of the polarizability of large oligomeric and polymeric systems is a field of intense investigation due to its direct relation with the design of new compounds for optics and photonics applications [1]. The interest brought about by large polymeric systems lies in the nonlinear increase, as chain length grows, of the component of the polarizability tensor directed along the polymeric backbone. In other words, the intrinsic polarizability of the chain, which is represented by its polarizability per unit cell, increases in the smallest chains, then saturates, and finally becomes constant for the longest chains. Such exaltation phenomena are more pronounced in conjugated systems as a result of electron delocalization along the polymer backbone. In directions transverse and perpendicular to the polymer chain, the electron cannot be delocalized to such an extent. The perpendicular and the transverse polarizability per unit cell values are thus smaller than the longitudinal ones that focus our attention on the investigation of systems presenting large linear and nonlinear response properties. In order to determine the characteristics and properties of polymeric systems, two general procedures can be followed. The first procedure consists of studying increasingly large oligomers built from the successive addition of the same monomer unit and of extrapolating these results to the infinite polymeric limit. The alternative procedure is to deal directly with the stereoregular periodic system by carrying out band-structure calculations.

In addition to many other groups in the past, we have tackled many aspects of such investigations of large oligomeric and polymeric systems. Besides the large amount of semiempirical calculations [2] performed on various extended systems of chemical interest, a few *ab initio* studies have been made [3–30]. In most of these studies, the static polarizability of increasingly large oligomeric systems has been evaluated at the coupled Hartree-Fock level. Such a Hartree-Fock *ab initio* approach presents a peculiar advantage because its accuracy can systematically be improved. Indeed, starting from the Hartree-Fock solution, one approaches the true results through enlarging the basis set and including electron correlation up to a higher order in electron-electron interaction.

To our knowledge, the first *ab initio* Hartree-Fock calculations on the polarizability of finite oligomeric chains have been carried out by Bodart *et al.* [4] with the Slater-type orbital built from three Gaussian functions (STO-3G) minimal atomic basis set on polyacetylene chains ranging from 2 to 20 carbon atoms and presenting various degrees of bond-length alternation. The same procedure has been applied to the study of hydrocarbon chains incorporating different cumulenic structures [5]. The polyacetylene chains, the π-conjugated prototype systems, have been studied at the coupled Hartree-Fock level by Hurst, Dupuis, and Clementi [6], who assessed the effects due to the choice of the atomic basis set, and by Champagne *et al.* [7], who investigated the effects of both the geometrical parameters and the atomic basis set. At the same level of theory, Chopra *et al.* have analyzed the (hyper) polarizabilities of the four smallest oligomers of polyacetylene, polyyne, and cumulene in terms of the polarization of the σ- and π-symmetry molecular orbitals [8]. Other π-conjugated polymers having a carbon backbone; polydiacetylene [9], polybutatriene [9], and more recently polyyne [10] chains have also been studied. The less alternating the bond-length values, the larger the electron delocalization and the larger the polarizability. Therefore, since the triple-bond-length value is small with respect to the double and single bond lengths, polyyne and polydiacetylene are the less polarizable of these π-conjugated systems. Theoretical calculations have dealt also with the polysilane chains [11] that present a real interest due to their σ-conjugated character. Indeed, the electron density of the higher-energy levels oriented along the polymeric chain and the diffuseness of the silicon atoms and their weak electronegativity confer on polysilane a large electron delocalization and therefore a longitudinal polarizability per unit cell that increases with chain length. Recently, the polarizability of increasingly large polythiophene chains has been investigated [12]. It has been shown that polythiophene is more polarizable than polydiacetylene, polyyne, and polysilane but less polarizable than polyacetylene and polybutatriene. All these calculations have been performed at the coupled Hartree-Fock level of approximation with atomic basis sets ranging from the minimal STO-3G to the split-valence 3-21G and 6-31G and to the more extended 6-31G*, 6-31G**, and 6-311G** atomic basis sets. From these works, one can describe the basis-set effects by saying that the addition of polarization and/or diffuse functions to a split-valence or double-ζ atomic basis set does not significantly change the longitudinal polarizability values per unit cell. As examples of this statement, it was found that the longitudinal polarizability per unit cell of polyacetylene [7] and polythiophene [12] obtained with the 3-21G atomic basis set already amounts to 87% and 86%, respectively, of the polarizability values calculated by using the medium-size polarized basis set designed by Sadlej [13] to obtain the best values of the polarizability. The importance of including the field-induced electron reorganizational effects in the polarizability calculations has been addressed in some of these studies [7,8,12,14–16]. The lack of reorganizational effects that characterized the uncoupled Hartree-Fock scheme leads to a polarizability underestimation value that is more marked as the electron delocalization along the polymer backbone increases. Grant and Pickup [17] analyzed further the coupled Hartree-Fock polarizability values of polyacetylene chains ranging from C_4H_6 to $C_{20}H_{24}$ with the 6-31G atomic basis set. They decomposed the field-induced electron relaxation terms into an interaction term that corresponds to the self-interaction of the perturbed density and the back polarization that is the polarization induced from the field arising from the perturbed electron density. In the case of the longitudinal polarizability tensor components, both the interaction and the back-polarizability terms have a larger amplitude than the direct, one-electron, uncoupled Hartree-Fock polarizability values, but they partially cancel each other, the positive interaction contribution being more important than the negative back-polarization term.

In order to get directly the asymptotic longitudinal polarizabilities per unit cell, we have developed polymeric techniques at both the coupled and the uncoupled Hartree-Fock levels of approximation. These techniques take advantage of the one-dimensional periodicity of these systems. At the uncoupled Hartree-Fock (UCHF) level, the polymeric technique [18] corresponds to the Genkin-Mednis procedure [19] of which the ground and excited states are represented by Slater determinants. This technique has already been applied to several steroregular polymers ranging from the molecular hydrogen chain models [20] and the prototypes of the saturated hydrocarbon chains (polyethylene) [18,21,24], of the unsaturated π-conjugated chains (polyacetylene) [22,24], and of the saturated σ-conjugated systems (polysilane) [18,22–24] to candidate systems for an application in nonlinear optics and photonics such as polythiophene, polypyrrole, etc. [22,24–26]. At the coupled Hartree-Fock level, we have adapted the random-phase approximation scheme to the periodic infinite systems and applied it to molecular hydrogen chain models [15], polyacetylene [7,27], polydiacetylene [27], polybutatriene [27], polyyne [27], polyethylene [16], and polysilane [16].

In order to improve the polarizability estimates, it is necessary to address the dynamic character of the polarizability and to take into account the coupling between the electronic and the nuclear motions that results in a vibrational contribution to the polarizability. A few investigations deal with the dynamic character of the electric-dipole polarizability of large systems. Karna *et al.* [28] have addressed the frequency-dependence effects on the polarizability of small oligomers of polyacetylene. In a recent study, we have analyzed that effect in finite and infinite chains of molecular hydrogen [29]. Moreover, the importance of the static vibrational contribution to the polarizability per unit cell of polyacetylene, polysilane, and polyethylene has been estimated within the double-harmonic-oscillator approximation [30]. It turns out that the vibrational contribution is negligible in the case of the polyethylene chains whereas it amounts to 10% of the electronic polarizability value for polyacetylene chains and it reaches 50% of the electronic polarizability in polysilane chains as a result of both σ conjugation and the large polarity of the Si-H bonds.

The other step for improving the polarizability estimates consists therefore in going beyond the Hartree-Fock level, that is, by taking into account electron correlation. Since we are dealing with increasingly large oligomeric chains, the procedure adopted should be size consistent, i.e., the computed properties should scale properly with the size of the system. A preliminary study has already been carried out on molecular hydrogen chain models at different levels of approximation to investigate the effects of including electron correlation with the Møller-Plesset treatments limited to second (MP2), the third (MP3), and the fourth (MP4) order in electron-electron interactions as well as with the coupled-cluster techniques including all double substitutions (CCD), all single and double substitutions (CCSD), and all single and double substitutions with a perturbational estimate of the connected triple excitations [CCSD(T)] [31]. These calculations were performed on model alternating hydrogen chains with bond-length values successively equal to 2 and 3 a.u. It has been shown that including electron correlation decreases the longitudinal polarizability values and that the electron-correlation effects are overemphasized when using a too small basis set. Besides, polarization functions and triple-ζ-type basis sets are required to give suitable polarizability estimates. In addition, within the Møller-Plesset treatment of electron correlation, the double substitutions present the largest electron-correlation correction to the coupled Hartree-Fock longitudinal polarizabilities per unit cell and, among these contributions, the third-order contribution is dominant if the atomic basis set is sufficiently extended. To our knowledge, the impact on the calculated polarizability values of polymeric chains of the chemical interest due to including electron correlation has only been addressed in the case of polyyne chains ranging from C_2H_2 to $C_{12}H_2$ with the multiconfiguration self-consistent field technique [32]. Indeed, the scarcity of such investigations is due to the tremendous computational efforts associated with the use of these correlated techniques.

In the present work, we extend our investigation of the electron-correlation effects on the asymptotic longitudinal polarizabilities per unit cell by considering the influence of the bond-length alternation. Section II briefly summarizes the theoretical background and the computational procedure that we have adopted. Section III presents the longitudinal static polarizability results for three types of H_2 chains. For the different cases, the longitudinal polarizability per unit cell have been extrapolated to the infinite chain limit. From these extrapolated asymptotic values, we have assessed the effects of including electron-correlation corrections within different techniques and the importance of the basis-set choice according to the amplitude of the bond-length alternation in the molecular hydrogen chain models. Then, using the breakdown of the Møller-Plesset contributions, we have studied the importance of the different classes of substitutions at different orders in the treatment of electron-electron interactions as a function of the systems and the atomic basis set.

II. THEORETICAL AND COMPUTATIONAL FRAMEWORKS

A. Hydrogen chain models

The longitudinal component of the static electric-dipole polarizability tensor of different molecular hydrogen chain models has been computed as a function of chain length. These structures represented in Fig. 1 present different bond-length alternation patterns. Many times in the past, hydrogen models have been used to explain new techniques and features because they foresaw real systems (see, for instance, Ref. [31] for a list of papers dealing with molecular, oligomeric, and polymeric hydrogen models). Indeed, in the case of hydrogen chains, by increasing the bond-length alternation, the system ranges from the regular metallic one-dimensional chain to the Peierls distorted semiconductor or insulator. In our study, by increasing bond-length alternation, the chains correspond to conjugated polymeric chains having different electron delocalization.

B. Hartree-Fock and electron-correlation methods

First, the polarizabilities are computed using the uncoupled and the coupled Hartree-Fock (CHF) procedures. The uncoupled Hartree-Fock values are straightforwardly obtained after the Hartree-Fock calculation of the electronic structure as a summation of one-electron quantities [14]. Indeed, the UCHF procedure consists of substituting in the exact summation over state expression of the polarizability [31] the Hartree-Fock Slater determinants as approximate wave functions, their associated energies being the sums of molecular-orbital energies. The evaluation of the CHF values requires an iterative and analytical solution of the coupled-perturbed Hartree-Fock (CPHF) equations that consists of computing the first derivative of the electron density matrix with respect to the external electrical field [34]. The CHF scheme includes the field-induced electron reorganizational effects in a way that is fully consistent in terms of adjustments in the average two-electron interactions. Therefore, it is said to be a *coupled* Hartree-Fock procedure whereas in the uncoupled Hartree-Fock procedure only field-induced one-electron effects are accounted for [35]. Two strategies have been adopted to include electron correlation. Electron correlation can be examined in the framework of many-body perturbation theory by adopting the Møller-Plesset partitioning [36]. This leads thus to successive electron-correlation corrections, namely, MP2, MP3, etc., which are consistent in electron-electron interaction through second, third, etc., order, respectively. Electron correlation can also be included by considering the coupled-cluster approach [37]. In this

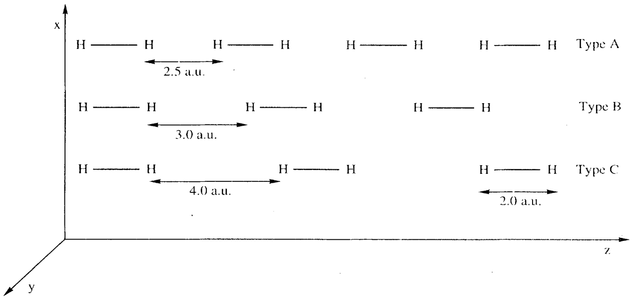


FIG. 1. Sketch of the different molecular hydrogen chain models.

work we have used the MP2, MP3, and MP4 techniques as well as the coupled-cluster technique, where included in the coupled-cluster ansatz are all double excitations, all single and double excitations, and all single and double excitations with a perturbational estimate of the connected triple excitations. These MØller Plesset and coupled-cluster treatments of electron correlation are size consistent, i.e., the properties properly evolve with the size of the chains.

By considering the MØller-Plesset treatment of electron correlation, the total energy can be decomposed in several terms that are characterized by their order in electron-electron interaction (subscript) and the class of substitutions used in the intermediate states (superscript; S stands for single substitutions, D for double substitutions, etc.). Hence the energy up to fourth order in electron-electron interactions [E(MP4)] can be rewritten

$$E(\mathrm{MP4})=E_{\mathrm{SCF}}+E_2^D+E_3^D+E_4^S+E_4^D+E_4^T+E_4^Q\ , \qquad (1)$$

where E_4^Q contains the contribution from the disconnected quadruple substitutions plus the renormalization. It is important to stress that each of these contributions is size extensive and therefore they can be analyzed independently. An expression similar to (1) can be written for the polarizability,

$$\alpha(\mathrm{MP4})=\alpha_{\mathrm{CHF}}+\alpha_2^D+\alpha_3^D+\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q\ . \qquad (2)$$

Since their evolution rates with chain length and their amplitudes are different, the relative contributions to the MP4 correction to the CHF values have been chosen to present this comparison. These values are given by the general expression

$$\%\alpha_I^X=\frac{\alpha_I^X}{\alpha_2^D+\alpha_3^D+\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q}\times 100\ . \qquad (3)$$

In the analysis of the electron-correlation effects, we chose in Sec. III the CHF values as references. This can appear incorrect from a mathematical point of view; the field-free molecular orbitals and their associated energies (that directly enter into the UCHF polarizability expression) are the basis of the MØller-Plesset and coupled-cluster approaches. In addition, there is no doubt that the random-phase approximation, which is another version of the coupled Hartree-Fock procedure, contains electron correlation [38]. Therefore one could say that the CHF procedure holds the lowest level of electron correlation. However, by analyzing the field-dependent Hartree-Fock equations, one sees that the CHF procedure merely represents a fully relaxed self-consistent field solution [14] and therefore can be used as electron-correlation-free reference in our analysis.

It is important to point out that the configuration-interaction truncated treatments should be avoided when dealing with large oligomers because the electron-correlation energy does not scale properly with the size of the system. Many other computational schemes exist to evaluate the electronic polarizability and we refer the interested reader to Ref. [31] and references cited therein for more details. Among these schemes, one can find analytical procedures that directly provide the polarizability without relying on finite-difference calculations.

C. Finite-field procedure

In order to calculate the electron-correlated polarizabilities, we have adopted the finite-field (FF) procedure that consists of computing the dipole moment or the total energy of a system under external electric fields of different amplitudes and considering a finite-difference formula [38]. When dealing with techniques including electron correlation where the dipole moment (computed from the wave function) is not directly available, the field-dependent total energy is used in the finite-difference formula

$$\begin{aligned}\alpha_{jj}&=-\left[\frac{\partial^2\mathcal{E}(E_j)}{\partial E_j^2}\right]_{\vec{E}=0}\\&=\lim_{E_j\to 0}-\frac{\mathcal{E}(E_j)+\mathcal{E}(-E_j)-2\mathcal{E}(0)}{E_j^2}\\&=\lim_{E_j\to 0}2\frac{\mathcal{E}(0)-\mathcal{E}(E_j)}{E_j^2}\end{aligned} \qquad (4)$$

in which the diagonal polarizability tensor elements are related to the second-order derivative of the total energy with respect to the external electrical field. The last equality of expression (4) holds only for centrosymmetric systems. The simplest level of application of the FF technique is in fact to use the Hartree-Fock energies where the field-induced relaxation of the orbitals has been considered self-consistently. This numerical scheme to compute the CHF polarizability is equivalent to the analytical coupled-perturbed Hartree-Fock procedure. In the same way as for the Hartree-Fock energies, Eq. (4) can be used for the correlated energies. Adopting a FF procedure allows the exploitation of theories and programs that have been developed and tuned for the usual correlation problem; the disadvantage of that is the need to carry out several calculations per polarizability calculation [see Eq. (4)] and the potential numerical errors associated with the derivative procedure. Many works have already been performed where the polarizability tensor has been obtained by numerical differentiation of the energy obtained at the MP2, MP3, MP4, CCD, CCSD, and CCSD(T) [40–42] levels.

D. Computational details

In this work, the minimal STO-3G [43] and double-ζ (3)-21G [44] atomic basis sets have been chosen as well as the double-ζ plus polarization (6)-31G(*)* [45] and triple-ζ plus polarization (6)-311G(*)* [46] atomic basis sets. The parentheses in these basis-set notations indicate the absence of core functions and core electrons for the hydrogen atom. The polarizability calculations performed at the UCHF, CHF, MP2, MP3, MP4, CCD, CCSD, and CCSD(T) levels of approximation have been carried out by using the GAUSSIAN92 computer program [47] of which some of the standard threshold conditions have been tightened, i.e., 10^{-10} a.u. for the two-electron integral cutoff and 10^{-10} for the requested convergence on the density-matrix elements. In the coupled-cluster calculations, the convergence threshold on the energy has been fixed at 10^{-10} a.u. These threshold decreases are necessary to meet a 10^{-3}-a.u. accuracy [48] on the polarizability values obtained from the finite-field procedure based on Eq. (4). Lowering these thresholds as we did is necessary to avoid any oscillatory behavior of the polarizability per unit cell values as the chain length increases, which would make difficult the extrapolation procedure. At the coupled Hartree-Fock level, the GAUSSIAN92 program follows the CPHF analytical procedure in which the requested convergence on the Z vector is 10^{-11} [47]. In the other cases [MP2, MP3, MP4, CCD, CCSD, and CCSD(T)], the adopted finite-field procedure employs, in addition to calculations at zero-field amplitude, electric fields of 0.0016 a.u. (8.23×10^8 V/m) and 0.0032 a.u. (16.46×10^8 V/m). These amplitudes have been chosen to avoid numerical instability in the finite difference and to ensure a suitable use of the finite-difference formula in order to evaluate correctly the derivative [48]. Indeed, if the field amplitude is too large, the contaminations from the higher-order hyperpolarizabilities increase whereas if the field amplitude is too small, the number of significant digits in the dipole or energy differences [Eq. (4)] decreases. Romberg's procedure [49] is used to improve the finite-derivative technique. In this case where three field

TABLE I. Longitudinal polarizability values of the A and the C types of molecular hydrogen model chains as a function of the number of structural H_2 units computed by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*] at the UCHF and the CHF levels of approximation. All values are given in a.u. (1.0 a.u. of polarizability is equal to 1.6488×10^{-41} $C^2\,m^2\,J^{-1}=0.148\,18$ Å^3).

	UCHF		CHF			UCHF		CHF	
N	Type A	Type C	Type A	Type C	N	Type A	Type C	Type A	Type C
		STO-3G					(6)-31G(*)*		
1	5.736	5.736	5.812	5.812	1	9.257	9.257	11.312	11.312
2	17.793	12.331	19.779	13.373	2	24.879	19.737	33.827	26.909
3	33.186	18.961	39.965	21.234	3	44.627	30.327	66.419	43.712
4	50.143	25.592	64.338	29.171	4	66.039	40.919	106.034	60.900
5	67.769	32.223	91.319	37.138	5	88.247	51.512	150.585	78.244
6	85.666	38.853	119.866	45.117	6	110.759	62.106	198.394	95.661
7	103.666	45.484	149.345	53.105	7	133.396	72.699	248.360	113.119
8	121.705	52.115	179.385	61.095	8	156.078	83.291	299.752	130.600
9	139.757	58.745	209.768	69.089	9	178.778	93.884	352.097	148.096
10	157.815	65.376	240.369	77.085	10	201.483	104.477	405.092	165.603
11	175.875	72.007	271.113	85.082	11	224.191	115.070	458.536	183.116
12	193.935	78.638	301.953	93.081	12	246.900	125.663	512.299	200.635
13	211.995	85.268	332.860	101.080	13	269.609	136.256	566.291	218.158
14	230.056	91.899	363.899	109.079	14	292.318	146.849	620.451	235.684
15	248.116	98.530	394.806	117.080	15	315.027	157.442	674.737	253.212
16	266.177	105.161	425.824	125.080	16	337.736	168.035	729.120	270.743
17	284.237	111.791	456.863	133.081	17	360.445	178.628	783.577	288.274
18	302.298	118.422	487.918	141.082	18	383.154	189.221	838.094	305.808
		(3)-21G					(6)-311G(*)*		
1	9.179	9.179	10.852	10.852	1	9.726	9.726	12.311	12.311
2	24.775	19.802	32.783	26.166	2	25.728	20.103	35.868	28.062
3	44.603	30.525	64.677	42.686	3	45.700	30.652	69.407	45.019
4	66.166	41.253	103.551	59.594	4	67.247	41.211	109.812	62.351
5	88.562	51.980	147.315	76.657	5	89.554	51.775	155.028	79.836
6	111.282	62.708	194.309	93.793	6	112.135	62.340	203.392	97.394
7	134.136	73.436	243.436	110.969	7	134.839	72.906	253.851	114.991
8	157.039	84.163	293.969	128.167	8	157.582	83.471	305.687	132.611
9	179.961	94.891	345.441	145.380	9	180.344	94.037	358.450	150.246
10	202.890	105.618	397.550	162.604	10	203.110	104.602	411.842	167.892
11	225.821	116.346	450.100	179.834	11	225.879	115.168	465.672	185.544
12	248.753	127.073	502.960	197.070	12	248.649	125.733	519.812	203.202
13	271.686	137.801	556.044	214.309	13	271.419	136.299	574.176	220.864
14	294.618	148.528	609.291	231.551	14	294.189	146.864	628.706	238.528
15	317.551	159.256	662.662	248.796	15	316.959	157.430	683.359	256.196
16	340.484	169.983	716.126	266.042	16	339.729	167.995	738.107	273.865
17	363.416	180.711	769.663	283.291	17	362.499	178.560	792.929	291.535
18	386.349	191.438	823.256	300.540	18	385.269	189.126	847.809	309.208

amplitudes are used, the next nonzero term in the series expansion of the energy with respect to the field amplitude is eliminated. In other words, since the first (β) and third (δ) hyperpolarizabilities are zero due to centrosymmetry, the first term that contaminates the polarizability value is proportional to the fourth hyperpolarizability (ε) (which contributes to the energy by a term at the power 6 in the field amplitude). In fact, this technique corresponds exactly to the one proposed by Bartlett and Purvis [42] and used by Sim *et al.* [50].

TABLE II. Longitudinal polarizability values of the *A* and the *C* types of molecular hydrogen model chains as a function of the number of structural H_2 units computed by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311(G)(*)*] at the MP2, the MP3, and the MP4 levels of approximation. All the values are given in a.u.

	MP2		MP3		MP4	
N	Type *A*	Type *C*	Type *C*	Type *A*	Type *A*	Type *C*
			STO-3G			
1	5.153	5.153	4.691	4.691	4.485	4.485
2	17.141	11.666	15.139	10.495	14.297	9.997
3	34.075	18.394	29.241	16.454	27.255	15.641
4	54.222	25.174	45.389	22.449	41.814	21.314
5	76.313	31.974	65.582	28.456	57.079	26.996
6	99.532	38.783	80.273	34.469	72.605	32.683
7	123.396	45.596	98.186	40.485	88.197	38.373
8	147.628	52.412	116.191	46.504	103.779	44.064
9	172.076	59.231	134.232	52.523	119.330	49.757
10	196.654	66.050	152.282	58.544	134.846	55.450
			(3)-21G			
1	9.830	9.830	9.144	9.144	8.804	8.804
2	29.802	23.511	27.564	21.674	26.469	20.787
3	58.883	38.202	53.784	35.053	51.311	33.510
4	94.458	53.202	85.264	48.635	80.883	46.443
5	134.682	68.319	120.337	62.325	113.624	59.450
6	178.014	83.492	157.703	76.056	148.350	72.492
7	223.402	98.694	196.520	89.808	184.309	85.552
8	270.135	113.913	236.243	103.573	221.021	98.623
9	317.753	129.143	276.540	117.347	258.195	111.700
10	365.962	144.381	317.202	131.126	295.656	124.782
			(6)-31G(*)*			
1	10.532	10.532	10.120	10.120	9.915	9.915
2	32.045	25.001	30.847	23.939	30.248	23.417
3	63.600	40.575	60.874	38.766	59.571	37.877
4	102.483	56.491	97.535	53.899	95.301	52.626
5	146.735	72.540	138.964	69.150	135.647	67.486
6	194.648	88.652	183.593	84.456	179.106	82.398
7	245.034	104.797	230.356	99.792	224.645	97.337
8	297.067	120.963	278.521	115.145	271.554	112.292
9	350.204	137.141	327.617	130.510	319.369	127.258
10	404.091	153.327	377.337	145.882	367.790	142.230
			(6)-311G(*)*			
1	11.575	11.575	11.228	11.228	11.052	11.052
2	34.611	26.500	33.647	25.681	33.153	25.259
3	67.865	42.568	65.669	41.205	64.640	40.497
4	108.550	58.983	104.549	57.050	102.856	56.045
5	154.700	75.536	148.396	73.023	145.969	71.714
6	204.563	92.154	195.576	89.055	192.392	87.441
7	256.956	108.807	245.008	105.119	241.061	103.197
8	311.035	125.481	295.926	121.202	291.218	118.972
9	366.254	142.168	347.843	137.298	342.375	134.758
10	422.248	158.864	400.433	153.401	394.204	150.553

TABLE III. Longitudinal polarizability values of the *A* and the *C* types of molecular hydrogen model chains as a function of the number of structural H_2 units computed by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*] at the CCD, the CCSD, and the CCSD(T) levels of approximation. All values are given in a.u.

	CCD		CCSD		CCSD(T)	
N	Type *A*	Type *C*	Type *A*	Type *C*	Type *A*	Type *C*
			STO-3G			
1	4.230	4.230	4.433	4.433	4.433	4.433
2	13.160	9.349	14.244	9.922	14.292	9.939
3	24.384	14.564	27.309	15.555	27.548	15.597
4	36.381	19.797	42.111	21.222	42.737	21.290
5	48.411	25.037	57.751	26.900	58.953	26.995
6	60.212	30.280	73.769	32.584	75.697	32.707
7	71.744	35.524	89.947	38.272	92.710	38.422
8	83.044	40.770	106.191	43.961	109.862	44.140
9	94.169	46.016	122.462	49.652	127.090	49.858
10	105.166	51.263	138.743	55.343	144.359	55.577
			(3)-21G			
1	8.382	8.382	8.619	8.619	8.619	8.619
2	24.956	19.643	25.856	20.351	25.947	20.398
3	47.520	31.509	49.771	32.794	50.201	32.920
4	73.551	43.533	77.864	45.442	78.972	45.657
5	101.574	55.611	108.592	58.164	110.725	58.474
6	130.618	67.713	140.869	70.922	144.330	71.329
7	160.155	79.829	174.054	83.698	179.078	84.203
8	189.905	91.952	207.766	96.486	214.530	97.089
9	219.732	104.081	241.790	109.281	250.420	109.982
10	249.572	116.212	276.001	122.080	286.587	122.881
			(6)-31G(*)*			
1	9.690	9.690	9.756	9.756	9.756	9.756
2	29.448	22.811	29.632	22.990	29.719	23.026
3	57.377	36.805	57.812	37.122	58.253	37.221
4	90.783	51.057	91.604	51.524	92.751	51.696
5	127.890	65.409	129.224	66.031	131.445	66.279
6	167.345	79.806	169.298	80.586	172.914	80.912
7	208.287	94.228	210.946	95.168	216.209	95.571
8	250.165	108.664	253.596	109.765	260.695	110.247
9	292.639	123.110	296.894	124.372	305.962	124.933
10	335.503	137.562	340.616	138.985	351.752	139.625
			(6)-311G(*)*			
1	10.867	10.867	10.886	10.886	10.886	10.886
2	32.405	24.774	32.443	24.804	32.577	24.846
3	62.495	39.634	62.613	39.680	63.208	39.793
4	98.382	54.777	98.644	54.842	100.104	55.036
5	138.253	70.032	138.721	70.117	141.458	70.395
6	180.675	85.339	181.407	85.445	185.774	85.809
7	224.754	100.673	225.798	100.802	232.075	101.252
8	269.894	116.025	271.288	116.176	279.682	116.712
9	315.728	131.387	317.500	131.561	328.159	132.184
10	361.623	146.757	363.795	146.953	376.821	147.663

TABLE IV. Asymptotic longtudinal polarizabilty per unit cell of molecular hydrogen chain model A computed at various levels of approximation [UCHF, CHF, MP2, MP3, MP4, CCD, CCSD, and CCSD(T)] by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*] (see the text for a description of the extrapolation procedures). The values given in italics correspond to the relative electron-correlation correction to the polarizabilty, i.e., the difference (in percent) between the correlated and the CHF values. The last part of the table lists in percent the polarizability changes by going from smaller basis sets to larger basis sets. All values are given in a.u.

Type A	UCHF	CHF	MP2	MP3	MP4	CCD	CCSD	CCSD(T)
STO-3G (I)	18.060	31.104	24.863	18.173	15.468	10.666	16.354	17.412
	±0.001	±0.002	±0.003	±0.031	±0.006	±0.018	±0.001	±0.016
			−20.1	*−41.6*	*−50.3*	*−65.7*	*−47.4*	*−44.0*
(3)-21G (II)	22.933	53.786	49.772	38.266	38.266	29.837	34.721	36.803
	±0.001	±0.001	±0.027	±0.013	±0.013	±0.005	±0.016	±0.017
			−7.5	*−22.8*	*−28.9*	*−44.5*	*−35.4*	*−31.6*
(6)-31G(*)* (III)	22.709	54.715	55.775	51.355	50.016	43.870	44.812	47.226
	±0.001	±0.001	±0.002	±0.013	±0.017	±0.003	±0.024	±0.031
			+1.9	*−6.1*	*−9.4*	*−19.8*	*−18.1*	*−13.7*
(6)-311G(*)* (IV)	22.770	55.079	57.958	54.332	53.564	47.594	48.022	50.632
	±0.001	±0.001	±0.010	±0.008	±0.018	±0.006	±0.009	±0.019
			+5.0	*−1.4*	*−2.8*	*−13.6*	*−12.8*	*−8.1*
II→IV	−0.7	+2.4	+16.4	+30.9	+40.0	+59.5	+38.3	+37.6
III→IV	+0.3	+0.7	+3.9	+3.9	+9.3	+8.5	+7.2	+7.2

E. Extrapolation procedure

In order to determine the asymptotic longitudinal polarizability per unit cell, one considers the evolution of the variation of the longitudinal polarizability between consecutive oligomers $\alpha_{zz}(N)-\alpha_{zz}(N-1)$ as a function of chain length because such a formula has the advantage of reducing the chain-end effects. Since for the largest chains that can be treated with the techniques including electron correlation the variation of $\alpha_{zz}(N)-\alpha_{zz}(N-1)$ is still important, one has to extrapolate in order to predict the polymeric results. This is particularly the case for the less alternating chains. In order to improve the extrapolation procedure, we consider the evolution with chain length of the ratios α (with electron correlation)/α(CHF) that converge faster than both its components [51]. Since the CHF calculations can be performed on larger oligomeric chains, the extrapolated CHF values are very accurate and the extrapolated values including electron correlation can be obtained with improved accuracy. The CHF extrapolated values are obtained by fitting the parameters of the equation

$$\alpha_{zz}^{\mathrm{CHF}}(N)-\alpha_{zz}^{\mathrm{CHF}}(N-1)=a-be^{-cN} \qquad (5)$$

TABLE V. Asymptotic longitudinal polarizability per unit cell of molecular hydrogen chain model B computed at various levels of approximation (UCHF, CHF, MP2, MP3, MP4, CCD, CCSD, and CCSD(T)] by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*] (see the text for a description of the extrapolation procedures). The values given in italics correspond to the relative electron-correlation correction to the polarizability, i.e., the difference (in percent) between the correlated and the CHF values. The last part of the table lists in percent the polarizability changes by going from smaller basis sets to larger basis sets. All values are given in a.u.

Type B	UCHF	CHF	MP2	MP3	MP4	CCD	CCSD	CCSD(T)
STO-3G (I)	10.144	14.604	11.911	9.839	9.050	7.881	9.278	9.452
	±0.001	±0.002	±0.002	±0.002	±0.002	±0.003	±0.003	±0.002
			−18.4	*−32.6*	*−38.0*	*−46.0*	*−36.5*	*−35.3*
(3)-21G (II)	14.547	28.305	25.309	22.308	20.907	18.611	20.098	20.561
	±0.001	±0.005	±0.005	±0.005	±0.005	±0.005	±0.005	±0.005
			−10.6	*−21.2*	*−26.1*	*−34.2*	*−29.0*	*−27.4*
(6)-31G(*)* (III)	14.347	28.502	27.270	25.663	24.943	23.460	23.726	24.176
	±0.001	±0.002	±0.003	±0.003	±0.002	±0.002	±0.002	±0.002
			−4.3	*−10.0*	*−12.5*	*−17.7*	*−16.8*	*−15.2*
(6)-311G(*)* (IV)	14.361	28.602	28.198	27.010	26.508	25.105	25.128	25.666
	±0.001	±0.004	±0.004	±0.004	±0.004	±0.004	±0.004	±0.004
			−1.4	*−5.6*	*−7.3*	*−12.2*	*−12.1*	*−10.3*
II→IV	−1.3	+1.0	+11.4	+21.1	+26.8	+34.9	+25.0	+24.8
III→IV	0.1	+0.4	+3.4	+5.2	+6.3	+7.0	+5.9	+6.2

TABLE VI. Asymptotic longitudinal polarizability per unit cell of molecular hydrogen chain model C computed at various levels of approximation [UCHF, CHF, MP2, MP3, Mp4, CCD, CCSD, and CCSD(T)] by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*] (see the text for a description of the extrapolation procedures). The values given in italics correspond to the relative electron-correlation correction to the polarizability, i.e., the difference (in percent) between the correlated and the CHF values. The last part of the table lists in percent the polarizability changes by going from smaller basis sets to larger basis sets. All values are given in a.u.

Type C	UCHF	CHF	MP2	MP3	MP4	CCD	CCSD	CCSD(T)
STO-3G (I)	6.631	8.003	6.826	6.026	5.698	5.252	5.697	5.725
	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
			−14.7	*−24.7*	*−28.8*	*−34.4*	*−28.8*	*−28.5*
(3)-21G (II)	10.728	17.256	15.266	13.814	13.104	12.152	12.822	12.920
	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
			−11.5	*−19.9*	*−24.1*	*−29.6*	*−25.7*	*−25.1*
(6)-31G(*)* (III)	10.593	17.540	16.216	15.400	14.999	14.478	14.640	14.719
	±0.001	±0.002	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
			−7.5	*−12.2*	*−14.5*	*−17.5*	*−16.5*	*−16.1*
(6)-311G(*)* (IV)	10.565	17.682	16.730	16.135	15.826	15.401	15.423	15.511
	±0.001	±0.004	±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
			−5.4	*−8.7*	*−10.5*	*−12.9*	*−12.8*	*−12.3*
II→IV	−1.5	+2.5	+9.6	+16.8	+20.8	+26.7	+20.3	+20.1
III→IV	−0.3	+0.8	+3.2	+4.8	+5.5	+6.4	+5.3	+5.4

to the molecular results, the asymptotic polymeric values being given by a. Five points associated with the five longest oligomers are used in these fittings and the accuracy on the extrapolated values is estimated by the fluctuation on the a value by comparison with the values associated with using the four largest oligomers in the fitting procedure. Then the extrapolated values including electron correlation are obtained after fitting the function

$$\frac{[\alpha_{zz}(N)-\alpha_{zz}(N-1)]^{\text{correlated}}}{[\alpha_{zz}(N)-\alpha_{zz}(N-1)]^{\text{CHF}}}=\frac{a-be^{-cN}}{1-de^{-fN}} \qquad (6)$$

to these ratios where the different rates of saturation of the polarizabilities calculated at different levels of approximation have been considered. The correlation-corrected asymptotic polarizability values per unit cell are then given by

$$\alpha_{zz}(\text{correlation})=\alpha_{zz}(\text{CHF})^{*}a \ . \qquad (7)$$

Eight points have been used in these fittings. The accuracy of a is given by the variation on a obtained when restricting the oligomeric results to the seven longest chains whereas the uncertainty is estimated by using the following expression defining the relation between the percent relative uncertainty of a product from the percent relative uncertainty of each element entering in the product:

$$\%\alpha_{zz}(\text{correlation})=\sqrt{[\%\alpha_{zz}(\text{CHF})]^2+(\%a)^2} \ . \qquad (8)$$

Many other forms for the fitting functions have been presented and used to extrapolate the polarizability and other properties of polymeric chains to the infinite chain limit. A power series of $1/N$ has already been proposed to extrapolate total and orbital energies of polyacetylene chains [52] and has been applied many times to fit the (hyper)polarizabilities of polymeric chains [9,11,53] or the logarithm [6] of these properties. Padé approximants with the formal variable $1/N$ have also been used [54]. With the exception of fitting the total energy per unit cell, which can formally be written in the form of a power series in $1/N$ [55], none of the fitting functions has presented an advantage. This is why we have chosen to retain the exponential form (5) that has been used many times in the past [7,12]. All the more, whatever the fitting function is, the same asymptotic value should be obtained as the chain length is sufficiently large. This last statement would thus suggest the use of more than one technique to assess the uncertainty due to extrapolation. This, however, was not the purpose of this work and we have chosen to restrict our fitting procedure to Eq. (5).

III. RESULTS AND DISCUSSION

A. Effects of the basis set size, the bond-length alternation, and the degree of inclusion of the electron correlation

The longitudinal polarizability values obtained with the various techniques and atomic basis sets are given in Tables I–III for the A and the C molecular hydrogen chain models. The corresponding results for the type-B system can be found in Ref. [31]. Tables IV–VI list the extrapolated longitudinal polarizability per unit cell values.

In our analysis of the asymptotic static longitudinal polarizability per unit cell, we choose the CHF values as a reference. By neglecting electron relaxation effects, the polarizability values are much smaller. Using the (6)-311G(*)* atomic basis set, the UCHF-to-CHF asymptotic longitudinal polarizability per unit cell ratios are 0.41, 0.50, and 0.60 for the A, B, and C chain types, respectively (see values in Tables IV–VI). Similar ratios (the variation of the ratio is of the order of 0.02) are obtained with the (3)-21G and the (6)-31G(*)* basis set whereas they increase (by 0.15–0.20) for the minimal STO-3G basis set.

In other words, the basis-set effects play a similar role in the UCHF-to-CHF ratios whatever the bond-length alternation. Similar statements have been obtained for the UCHF-to-CHF ratio between the *ab initio* asymptotic longitudinal polarizability per unit cell of polyethylene, polysilane, polyacetylene, and polydiacetylene: the more conjugated the systems, the smaller the UCHF-to-CHF ratio [7,16,27].

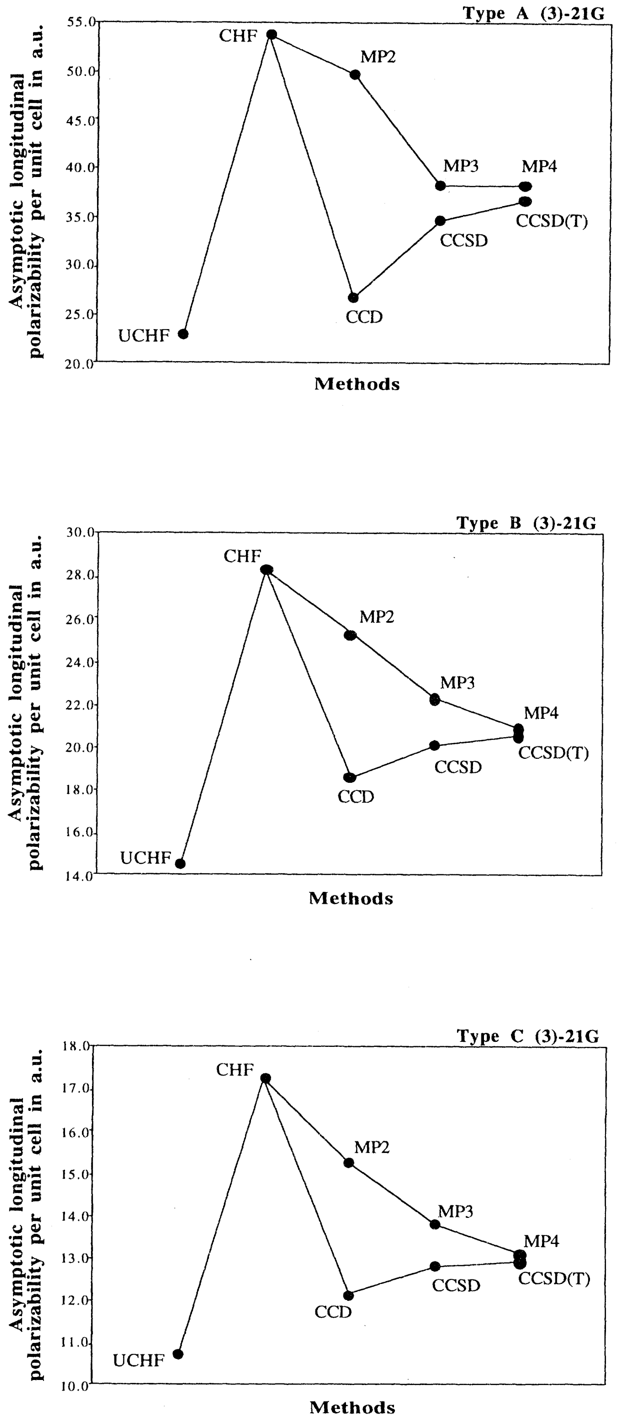


FIG. 2. Electron-correlation effects on the asymptotic longitudinal polarizability per unit cell of the different molecular hydrogen chain models computed with the (3)-21G atomic basis set. All values are given in a.u. The lines are included to help illustrate the trends.

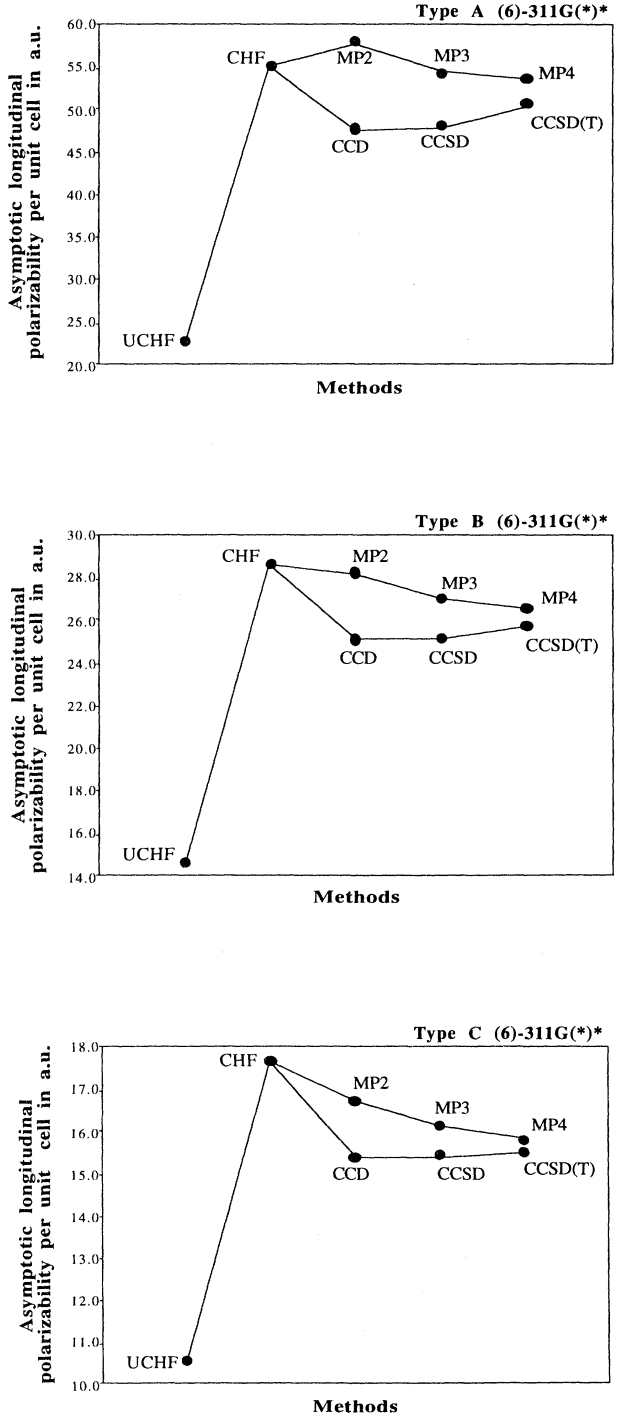


FIG. 3. Electron-correlation effects on the asymptotic longitudinal polarizability per unit cell of the different molecular hydrogen chain models computed with the (6)-311G(*)* atomic basis set. All values are given in a.u. The lines are included to help illustrate the trends.

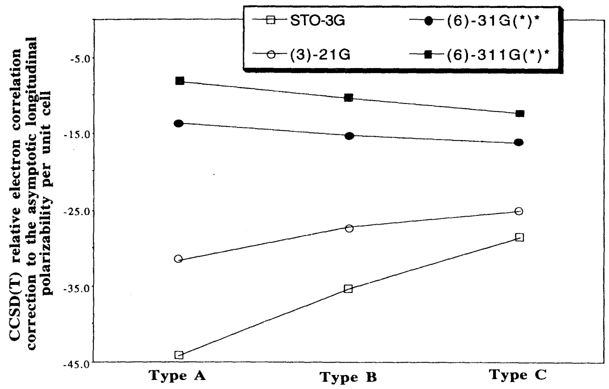


FIG. 4. Bond-length-alternation effect on the relative electron-correlation correction obtained with the CCSD(T) method to the asymptotic CHF polarizability per unit cell of infinite molecular hydrogen chain models. Types *A*, *B*, and *C* are associated with bond-length-alternation values of 0.5, 1.0, and 2.0 Å, respectively.

The electron-correlation corrections to the extrapolated CHF polarizabilities per unit cell of infinite molecular hydrogen chain models are all negative with the exception of the MP2 corrections on the chain of type *A* with the atomic basis sets including *p*-polarization functions. These corrections are given in italics for each basis set below the extrapolated values of the correlated polarizabilities in the central part of Tables IV–VI. The evolution of those asymptotic longitudinal polarizabilities per unit cell is represented in Figs. 2 and 3 as a function of the degree of inclusion of the electron correlation. The amplitude of these electron-correlation corrections increases by considering a higher order in the Møller-Plesset treatment, i.e., the polarizability value continues to decrease whereas the amplitude of that correction decreases slightly by considering more and more elaborate coupled-cluster *Ansätze,* i.e., enhancing the electron correlation[CCD versus CCSD and CCSD(T)] increases the polarizability. We can draw a first conclusion in stating that the CHF technique overestimates the asymptotic static longitudinal polarizability per unit cell of our model systems. This polarizability decrease due to electron correlation is attenuated by using more extended atomic basis sets (bottom of Tables IV–VI). In the peculiar case of the MP2 results of systems *A*, extending the basis set leads to a polarizability increase. Similar conclusions have already been drawn from molecular calculations [40,41]. Larger basis sets have thus to be employed when including electron-correlation effects on the polarizability of our systems, otherwise the correction is overestimated. These basis-set effects hold for the three H_2 chains under study and are enhanced in the case of the less alternating chains.

By considering the CCSD(T) technique, which we used as reference for the correlated treatments considered because it includes the largest amount of electron correlation, the relative amplitude of the electron-correlation correction to the CHF values (see in Tables IV–VI the values given in italics) increases with bond-length alternation using the basis sets with *p*-polarization functions [(6)-31G(*)* and (6)-311G(*)*] whereas that correction decreases with bond-length alternation using the STO-3G and the (3)-21G atomic basis sets (Fig. 4). These relative variations of the polarizability value due to including electron-correlation amount, with the (6)-311G(*)* atomic basis set, to −8.1%, −10.3%, and −12.3% for type *A*, *B*, and *C* systems, respectively, and, with the (3)-21G atomic basis set, to −31.6%, −27.4%, and −25.1%, respectively, for the same systems. The associated polarizability changes are −4.4, −2.9, and −1.2 a.u. for the (6)-311G(*)* basis set and −17.0, −7.8, and −4.3 a.u. for the (3)-21G basis set. Similar effects of the bond-length alternation and the atomic basis-set size are obtained at the various Møller-Plesset treatments of electron correlation with the exception of the (3)-21G/MP2 results that behave like the largest atomic basis sets (Tables IV–VI). In what concerns the CCD and the CCSD results, the larger the bond-length alternation, the smaller the relative electron correlation correction, with the exception of the inversion of the trend for type *B* and *C* systems with the (6)-311G(*)* atomic basis set. The general trend is thus a decrease of the relative magnitude of electron correlation corrections to the CHF values in the most conjugated chains if the basis set is sufficiently extended and if the electron correlation is treated at the Møller-Plesset or the CCSD(T) level; however, the general trend is a slight increase in the most conjugated chains if the CCD and the CCSD techniques are employed.

After focusing on the bond-length alternation effects,

TABLE VII. Contributions of the different classes of substitutions at the different orders in the Møller-Plesset treatment to the asymptotic longitudinal polarizability per unit cell of hydrogen chain models *A*. All values are given in a.u.

Type *A*	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
α_{SCF}	31.104	53.786	54.715	55.079
$\alpha_2^D=\alpha_2$	-6.241 ± 0.003	-4.197 ± 0.006	1.098 ± 0.022	2.926 ± 0.018
$\alpha_3^D=\alpha_3$	-6.756 ± 0.005	-8.111 ± 0.012	-4.484 ± 0.001	-3.656 ± 0.003
α_4^D	-3.746 ± 0.001	-5.097 ± 0.003	-2.715 ± 0.002	-2.204 ± 0.003
$\alpha_D(4)=\alpha_2^D+\alpha_3^D+\alpha_4^D$	-16.743 ± 0.009	-17.405 ± 0.021	-6.101 ± 0.025	-2.934 ± 0.024
α_4^S	0.698 ± 0.001	0.856 ± 0.008	0.540 ± 0.010	0.578 ± 0.009
α_4^T	0.518 ± 0.003	1.387 ± 0.011	1.718 ± 0.013	1.962 ± 0.103
α_4^Q	-0.089 ± 0.002	-0.553 ± 0.007	-0.891 ± 0.008	-1.106 ± 0.007
$\alpha_4=\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q$	-2.619 ± 0.007	-3.407 ± 0.029	-1.348 ± 0.033	-0.770 ± 0.116

TABLE VIII. Contributions of the different classes of substitutions at the different orders in the MØller-Plesset treatment to the asymptotic longitudinal polarizability per unit cell of hydrogen chain models *B*. All values are given in a.u.

Type *B*	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
α_{SCF}	14.04	28.305	28.502	28.602
$\alpha_2^D=\alpha_2$	-2.694 ± 0.001	-2.996 ± 0.001	-1.232 ± 0.001	-0.402 ± 0.003
$\alpha_3^D=\alpha_3$	-2.062 ± 0.004	-3.002 ± 0.003	-1.607 ± 0.004	-1.189 ± 0.004
α_4^D	-1.145 ± 0.001	-1.810 ± 0.001	-0.954 ± 0.002	-0.715 ± 0.001
$\alpha_D(4)=\alpha_2^D+\alpha_3^D+\alpha_4^D$	-5.901 ± 0.006	-7.808 ± 0.005	-3.793 ± 0.007	-2.306 ± 0.008
α_4^S	0.250 ± 0.001	0.220 ± 0.001	0.053 ± 0.001	0.036 ± 0.001
α_4^T	0.063 ± 0.003	0.237 ± 0.001	0.293 ± 0.001	0.351 ± 0.001
α_4^Q	0.051 ± 0.001	-0.040 ± 0.001	-0.115 ± 0.001	-0.176 ± 0.001
$\alpha_4=\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q$	-0.781 ± 0.006	-1.393 ± 0.004	-0.723 ± 0.005	-0.504 ± 0.004

we have also considered the effects of using different techniques. The results on the model system *C* clearly show that the difference between the electron-correlation corrections obtained at the CCSD and the CCSD(T) levels is very small; a similar conclusion holds for the difference between the CCD and the CCSD techniques if one excludes the small basis-set results. In addition, the more electron correlation included, the smaller the correction. Indeed, the variation of the relative electron-correlation correction is of the order of 0.5% between the CCSD(T) and the CCSD techniques and of the order of 1.0% between the CCSD and the CCD techniques for basis sets including *p*-polarization functions. If one considers the model system *B*, the difference amounts to 1.6% between the CCSD(T) and the CCD corrections and to 0.5% between the CCSD and the CCD corrections with the two most extended basis sets. This difference still increases when dealing with the least alternations case treated. It reaches 4.0% and 0.9% for the CCSD(T)-CCSD and the CCSD-CCD correction differences, respectively. Therefore, using suitable basis sets, the more elaborate the coupled-cluster technique, the smaller the corrections to the CHF overestimation. Moreover, the larger the bond-length alternation, the smaller the differences between the coupled-cluster corrections. In other words, by combining the previous comment with that of the preceding paragraph, one can state that the more conjugated the systems, the more electron correlation required to get suitable values, but the smaller the magnitude of the electron correlation correction.

In the framework of MØller-Plesset perturbation theory, the higher the order, the more negative the correction to the CHF values (Figs. 2 and 3). The relative importance of the MP3 correction with respect to the MP2 correction and of the MP4 correction with respect to the MP3 correction increases with the regularity of the chain, though the effective corrections with respect to the CHF values decrease with chain regularity. Indeed, using the (6)-311G(*)* atomic basis set, the MP4 results for system *A* differs only by 2.8% with respect to the CHF value whereas the gap for systems *B* and *C* are −7.3% and −10.5%, respectively (Tables IV–VI). Any other calculation with a smaller basis set will provide gaps between the CHF and the MP4 results [for instance, the (6)-31G(*)* results are −9.4%, −12.5%, and −14.5% for the *A*, the *B*, and the *C* systems, respectively), leading thus to a larger error in the case of the most alternating system. Using a less elaborate technique [for instance, MP3 with the (6)-311G(*)* atomic basis set] will give differences between the CHF and the MP3 techniques of −1.4%, −5.6%, and −8.7%, leading thus to similar error for the three types of bond-length alternations. The difference between the CCSD(T) and the MP4 techniques monotonically increases with both atomic basis-set size and regularity of the chain geometry. It ranges from 1% (0.2 a.u.) for the (3)-21G polarizability results of the *C*-type chain to 5.3% (2.9 a.u.) for the (6)-311G(*)* polarizability results of the *A*-type chain. As we will show further, the relative importance of the single

TABLE IX. Contributions of the different classes of substitutions at the different orders in the MØller-Plesset treatment to the asymptotic longitudinal polarizability per unit cell of hydrogen chain models *C*. All values are given in a.u.

Type *C*	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
α_{SCF}	8.003	17.256	17.540	17.682
$\alpha_2^D=\alpha_2$	-1.176 ± 0.001	-1.988 ± 0.001	-1.322 ± 0.001	-0.953 ± 0.002
$\alpha_3^D=\alpha_3$	-0.800 ± 0.001	-1.464 ± 0.001	-0.820 ± 0.002	-0.592 ± 0.002
α_4^D	-0.473 ± 0.001	-0.883 ± 0.003	-0.478 ± 0.001	-0.359 ± 0.009
$\alpha_D(4)=\alpha_2^D+\alpha_3^D+\alpha_4^D$	-2.449 ± 0.002	-4.335 ± 0.005	2.620 ± 0.004	-1.904 ± 0.013
α_4^S	0.107 ± 0.001	0.120 ± 0.001	0.020 ± 0.001	0.005 ± 0.001
α_4^T	0.007 ± 0.001	0.033 ± 0.001	0.037 ± 0.001	0.046 ± 0.001
α_4^Q	0.031 ± 0.001	0.038 ± 0.001	0.020 ± 0.001	$\in[-0.0005,0.0005]$
$\alpha_4=\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q$	-0.328 ± 0.001	-0.692 ± 0.004	-0.401 ± 0.002	-0.313 ± 0.011

and triple substitutions in the MP4 treatment and in the case of the least alternating chains must infer that higher-order terms for the single and triple substitutions should be included to properly account for the largest part of electron correlation.

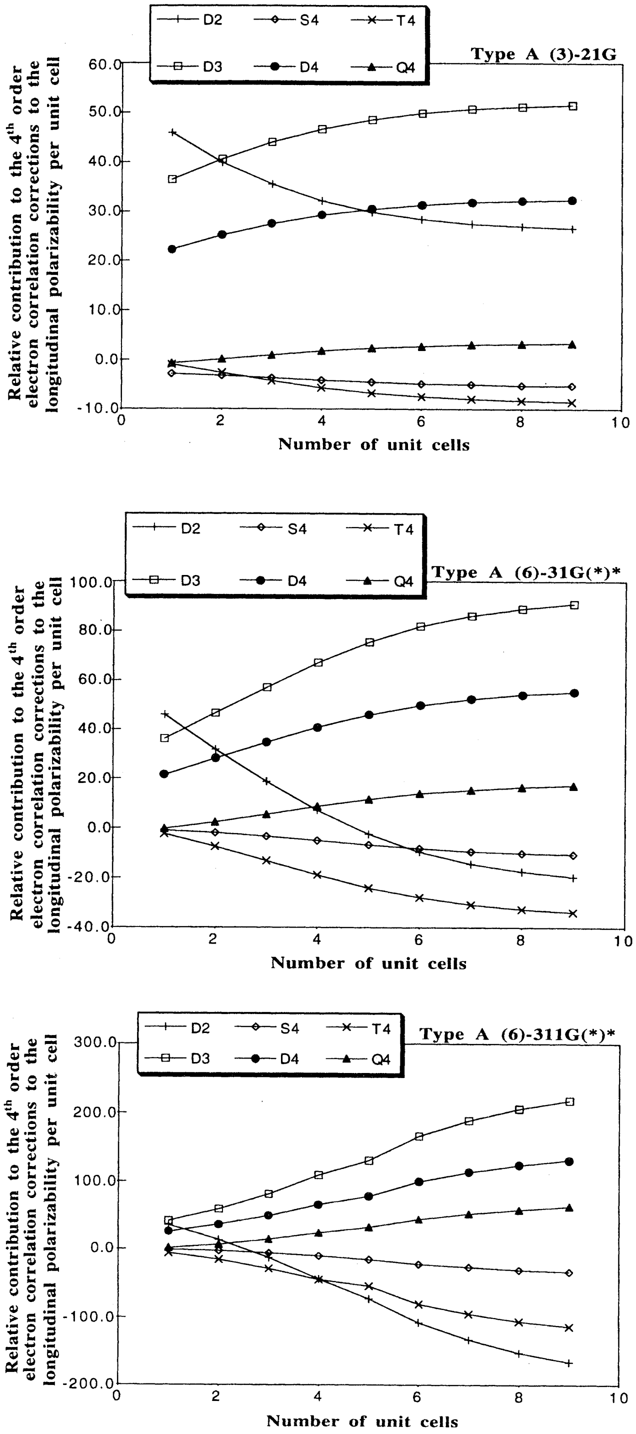


FIG. 5. Evolution with chain length of the relative contributions to the fourth-order electron-correlation corrections to the longitudinal polarizability per unit cell of molecular hydrogen chain models of type A as a function of the atomic basis set.

B. Breakdown of the Møller-Plesset contributions

We now turn to the breakdown of the Møller-Plesset contributions as a function of bond-length alternation, atomic basis-set size, and chain length. The contributions of the different classes of substitutions at different

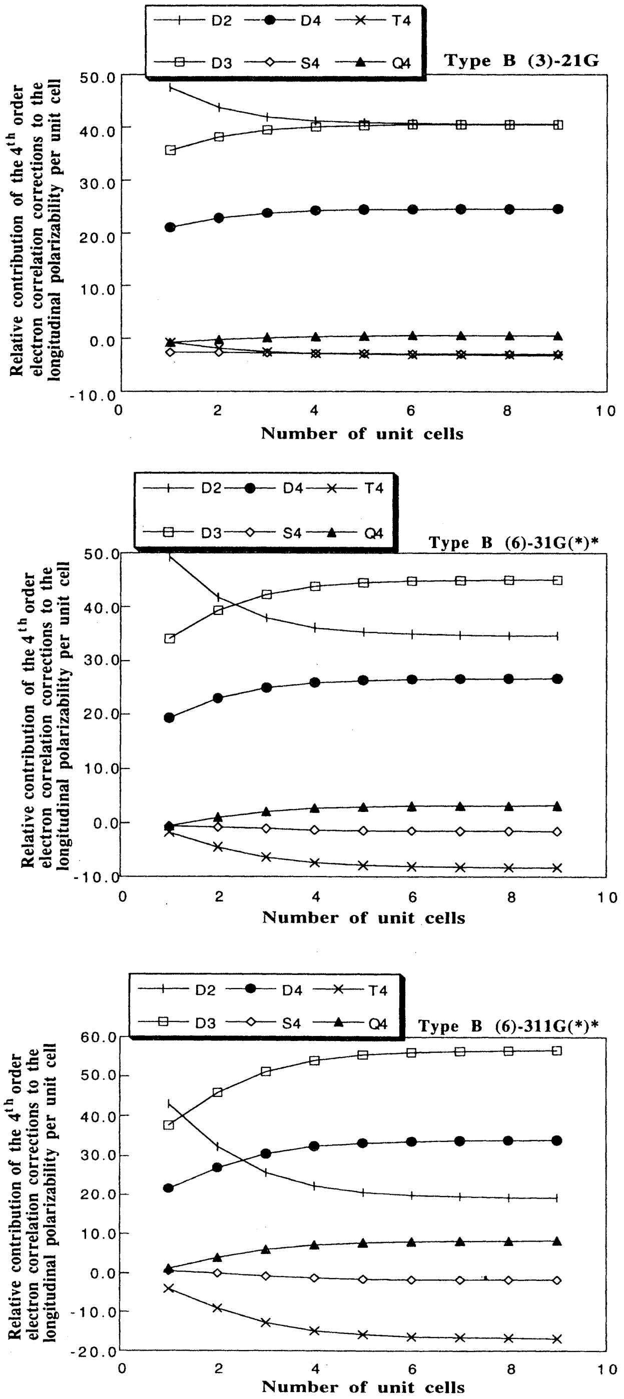
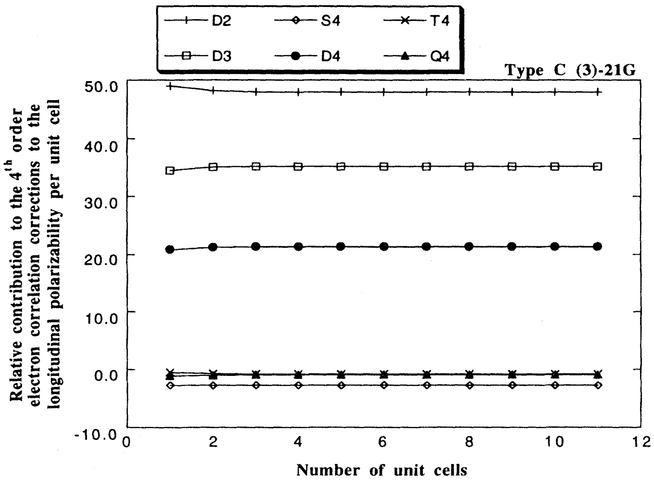


FIG. 6. Evolution with chain length of the relative contributions to the fourth-order electron-correlation corrections to the longitudinal polarizability per unit cell of molecular hydrogen chain models of type B as a function of the atomic basis set.

orders in the MØller-Plesset treatment to the asymptotic longitudinal polarizability per unit cell of the hydrogen chain models are given in Tables VII–IX.

The evolution of the relative contributions to the MP4 correction to the CHF values with chain length are depicted in Figs. 5–7 for the various types of H_2 chains and the different atomic basis sets. In the most alternating system, the various relative contributions to that MP4 correction per unit cell are nearly constant as chain length increases (Fig. 7) whatever the atomic basis set is. This is related to the fact that the different H_2 molecules do not interact significantly with each other. The second-, third-, and global fourth-order contributions are all negative (Table VII). Therefore, the more electron correlation included, the smaller the asymptotic longitudinal polarizability per unit cell. Most of the electron-correlation contribution comes from the double (D) substitutions. Among these double substitutions, the second-order term in electron-electron interaction is the largest; then comes the third- and finally the fourth-order term. Both the singles (S) and quadruples (Q) have decreasing contributions with the basis set size. With the (6)-311G(*)* atomic basis set, they nearly vanish. On the contrary, the contribution from the triples (T) grows with the size of the atomic basis set. All these S4, T4, and Q4 contributions are positive and at least one order of magnitude smaller than the D4 contribution. In this notation used in Figs. 5–7 the letter denotes the type of substitutions while the number signifies the order of electron correlation.



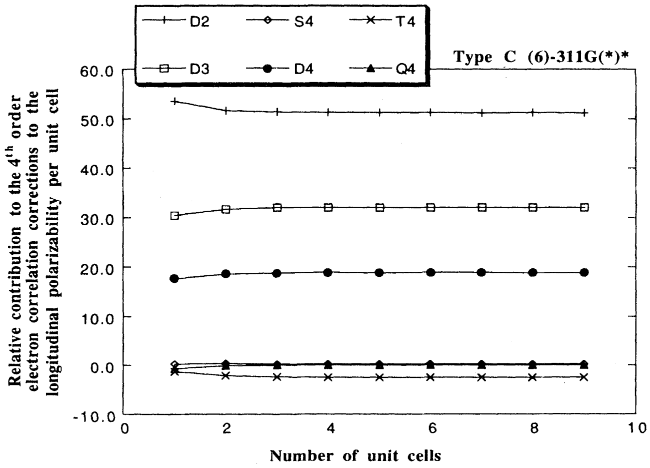


FIG. 7. Evolution with chain length of the relative contributions to the fourth-order electron-correlation corrections to the longitudinal polarizability per unit cell of molecular hydrogen chain models of type *C* as a function of the atomic basis set.

By considering chains of type *B*, all the second-, third-, and global fourth-order contributions are negative and the main part originates from the doubles (Table VIII). However, the third-order contribution becomes dominant for the (6)-31G(*)* and the (6)-311G(*)* atomic basis sets. By following with chain length the relative contributions to the α(MP4) electron correlation correction, one sees that all but D2 contributions increase with chain length (Fig. 6). The decrease of the D2 contribution is more important using more extended basis sets. As a consequence, using the STO-3G and the 3-21G basis sets, the order of decreasing importance is D2, D3, and D4; for the (6)-31G(*)* and (6)-311G(*)* atomic basis sets, the second-order contribution is the largest in the smallest chains, whereas for the longest chains, the orders of decreasing importance are D3, D2, and D4 and D3, D4, and D3 for the (6)-31G(*)* and the (6)-311G(*)* atomic basis sets, respectively (Fig. 6). In the same way as for the *C* systems, the S4 contribution to the asymptotic longitudinal polarizability per unit cell decreases with basis-set size whereas the T4 contribution increases. Both are positive, as for the *C* system. The contribution Q4 is negative (with the exception of the STO-3G basis set) and decreases with the size of the basis set. The relative importance of the nondouble substitutions S4, T4, and Q4 increases by going towards less alternating systems, but their relative importance is damped by a partial cancellation between S4, T4, and Q4. By considering the (6)-311G(*)* atomic basis sets, S4 and Q4 are negligible while T4 is $\frac{1}{10}$ of D4 for the type-*C* system; for system type *B*, S4 amounts to 25% of Q4 and T4 to 50%, while S4 is still negligible.

For the less alternating systems, the electron-correlation contributions of the different classes of substitutions at the different orders are larger than for the systems of type *B* and *C*. By considering Fig. 5 for the (6)-311G(*)* atomic basis set, we see that for the smallest chains, the double substitutions present the dominant contribution to the α(MP4) correction to α(CHF) whereas, as the chain length grows, the relative importance of the single, triple, and quadruple contributions increases. In this way, for the longest and least alternating chains, all the contributions have nearly the same order of magnitude and strongly cancel each other. Indeed the sum of the absolute values of the different contributions to the asymptotic values amount to 12.4 a.u. for a global effect of 1.5 a.u. by using the (6)-311G(*)* atomic basis set on system *A*. For comparison, by using the (6)-311G(*)* atomic basis set, these values amount to 2.9 a.u. for a global effect of 2.1 a.u. and to 1.9 a.u. for a global effect of 1.8 a.u. for the *B* and *C* systems, respectively.

Using the two largest atomic basis sets, the T4 contribution is very important with respect to the total fourth-order contribution and also with respect to the D4 contribution, which presents the largest fourth-order contribution. As a consequence, in that case of estimating the polarizabilities of H_2 chains of type A, a MP4(SDQ) (fourth-order MØller-Plesset treatment without the contribution from the triple substitution) treatment is certainly not better than a MP3 treatment of electron correlation for estimating the polarizabilities of H_2 chains. With the exception of D2, all the relative contributions increases with chain length. Using the (3)-21G basis set, the relative contribution D2 decreases (Fig. 5). Using the (6)-31G(*)* basis set, the D2 contribution decreases, changes of sign, and then increases. In the case of the (6)-311G(*)* atomic basis set, that increase is so large that D2 has a similar amplitude to the largest contribution (D3) and a larger amplitude than D4 but with opposite sign.

IV. CONCLUSIONS

Our calculations of the asymptotic static longitudinal polarizability per unit cell of periodic infinite molecular hydrogen chain models with different bond-length alternation, different correlation treatments, and different atomic basis sets have tried to give some insight into the question of knowing up to what order in electron-electron interactions and with what size of atomic basis set one should work to correctly estimate the static polarizabilities of polymeric systems. These results have also pointed out the importance of developing techniques based on the periodic infinite systems to get these asymptotic values directly.

From our results on the molecular hydrogen chain models, we can foresee that an equivalent description of the electron correlation effects on the static longitudinal polarizability per unit cell of polyethylene chains would require a less extended basis set than for polyacetylene chains since it is well known that polyacetylene is a π-conjugated system presenting an important electron delocalization whereas polyethylene is the prototype of the saturated hydrocarbon chains. In addition, the electron-correlation correction on polyacetylene chains should be smaller than in polyethylene, provided a sufficiently large atomic basis set is used and electron correlation is included up to a sufficiently high order in electron-electron interactions. Work is now in progress to verify this assumption.

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