PHYSICAL REVIEW A VOLUME 52, NUMBER 1 JULY 1995

Electron-correlation effects on the static longitudinal polarizability of polymeric chains

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(Received 18 October 1994)

Ab initio calculations of the static longitudinal polarizability of molecular hydrogen model chains have been performed at different levels of approximation to investigate the effects of including electron correlation. Unlike uncoupled and coupled Hartree-Fock calculations for which a split-valence atomic basis set already provides suitable longitudinal polarizability estimates, the techniques of the Møller-Plesset partitioning leading to successive electron corrections, namely, MP2, MP3, and MP4, and the coupled-cluster ansatz including all double excitations, all single and double excitations, and all single and double excitations as well as a perturbational estimate of the connected triple excitations require at least additional polarization functions and a triple-ζ-type basis set in order to give suitable polarizability values. It has also 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. Within the Møller-Plesset treatment of electron correlation, the relative importance of the different orders and the different classes of substitutions used in the intermediate states has been investigated. The double substitutions present the largest electron correlation correction to the coupled Hartree-Fock longitudinal polarizabilities per unit cell. If the atomic basis set is sufficiently extended, the third-order contribution is dominant.

PACS number(s): 31.15.Ar, 31.15.Dv, 31.15.Md

I. INTRODUCTION

Using quantum-chemical methods, considerable research has been directed recently toward predicting and understanding the linear (polarizability α) and nonlinear (second hyperpolarizabilty γ) responses of stereoregular conjugated polymeric systems to applied external electric fields (β, the first hyperpolarizability, is generally zero for these systems as a consequence of their symmetry) [1]. From deducing structure-property relationships, these quantum-chemical predictions can help in the elaboration of new compounds that would present the largest hyperpolarizabilities. Nowadays, the investigation of large molecular and polymeric systems presenting large nonlinear effects is hindered by the complexity and high sensitivity of the calculations of the second hyperpolarizabilities, and the related substantial computational task. Indeed, γ depends strongly upon the geometrical parameters, upon the method used (semiempirical or *ab initio*), upon the inclusion of electron correlation, and upon the atomic basis set used.

One means of investigation consists of using well-parametrized techniques that are able to reproduce in many cases the experimental results [2]. Another way consists of using, *ab initio,* the Hartree-Fock procedure, which possess a peculiar advantage because its accuracy can systematically be improved. Indeed, starting from the Hartree-Fock solution, by enlarging the basis set and by including via inadequate techniques electron correlation up to a higher order in electron-electron interaction, one approaches the true results. In this sense, the *ab initio* approach represents a consistent way of reaching the true electronic characteristics of compounds of interest. Due to tremendous computational costs, these *ab initio* approaches are often limited to the evaluation of the linear effects, the polarizabilities. To estimate the nonlinear responses, scaling laws that relate γ to α are used. Although large α are often associated with even larger γ, one should perform these scalings cautiously. Indeed, from the analysis of Nakano and Yamaguchi [3], it appears that the largest γ are always associated with the largest α, but the relationship does not necessarily hold in the opposite sense.

In this work, we adopt the *ab initio* approach to investigate the effects of electron correlation on the polarizability of large finite oligomeric systems of H_2 molecules. The study of increasingly large oligomeric chains built from the successive addition of the same monomeric unit, the unit cell, will provide the characteristics and properties of the infinite stereoregular polymeric chain. The interest brought about by large conjugated polymeric systems lies in the large increase of the component of the (hyper)polarizability tensors directed along the periodicity axis as chain length grows as a result of electron delocalization along the chain. In the smallest chains, the response per unit cell increases, then saturates, and finally becomes constant for the largest chains [4]. Since no similar evolution is possible for the directions perpendicular to the backbone of the chain, the longitudinal component is dominant and therefore of central interest in the investigation of systems presenting large linear and nonlinear response properties. Until now the *ab initio* evaluations of longitudinal polarizabilities per unit cell of large conjugated systems have been carried out at the coupled Hartree-Fock level by using split-valence basis sets [5–11]. The effects of increasing the atomic orbital

1050-2947/95/52(1)/178(11)/$06.00

basis set size have already been addressed in different works [6,10–12] and may be summarized by stating that adding polarization and/or diffuse functions to a split-valence or double-ζ atomic basis set does not change significantly the longitudinal polarizability values. For instance, in the evaluation of the longitudinal polarizability per unit cell of polyacetylene [12] and polythiophene [11], the use of the double-ζ 3-21G [46] atomic basis set provides already 87% and 86%, respectively, of the polarizability values obtained by using the medium-size polarized basis set designed by Sadlej [13] to reproduce the experimental values of the polarizability. The next step consists therefore in going beyond the Hartree-Fock level, that is, by taking into account electron correlation, in order to improve the polarizability estimates and to assess the electron correlation effects. Other investigations to improve the polarizability estimates consist of addressing the dynamic character of the polarizability and taking into account the coupling between the electronic and the nuclear motions that results in a vibrational contribution to the polarizability. At the coupled Hartree-Fock level, a study has recently been carried out to investigate the frequency dependence of the polarizability in large finite and infinite molecular hydrogen chains [14]. Very recently, the importance of the vibrational contribution to the polarizability per unit cell of polyacetylene, polysilane, and polyethylene has been assessed within the double harmonic-oscillator approximation [15].

Section II discusses the techniques used in this work among the various methods developed and available to compute the electronic contribution to the electric-dipole polarizability while taking into account the electron correlation up to different orders in electron-electron interactions. First, we use the Møller-Plesset treatment of the electron correlation up to fourth order in the electron-electron interactions [16]. The coupled-cluster ansatz [17] limited to the double substitutions, single and double substitutions, and single and double substitutions plus an estimate contribution of the connected triple substitutions has also been used. Both approaches to include electron correlation are size consistent and can thus treat increasingly large systems. The results and their discussion are presented in Sec. III. In order to highlight the effects, we use model molecular hydrogen chains, which, with the atomic and molecular hydrogen models, have already been used many times in quantum chemistry to demonstrate pedagogically new techniques and features. Indeed, by modifying the geometry (bond-length alternation) of the polymeric hydrogen chains, the system ranges, with increasing alternation, from the regular metallic one-dimensional chains to the Peierls distorted semiconductor and insulator. In this way, it foreshadows the polyacetylene chains possessing one π electron per carbon atom that can exhibit a metalliclike, semiconductor, and insulator behavior depending upon its bond-length alternation directly related to the doping rate and that also present very large optical responses in the pristine state [18]. Liegener [19], in his work applying third-order perturbation theory to infinite alternating hydrogen chains, gives a list of the papers dealing with such linear and cyclic, finite and infinite model systems, up to 1985. In 1986, Liegener and Ladik [20] computed the exciton spectra of infinite hydrogen chains. Moreover, simple hydrogen chains of various bond-length alternations present the slow convergence behavior of the exchange lattice summations of insulating and metallic one-dimensional periodic systems that appear in the Hartree-Fock band-structure calculations. Different approaches to evaluate exactly the exchange terms have been proposed and applied to these model chains [21]. The first *ab initio* calculations of the longitudinal polarizabilities per unit have been computed for hydrogen chains within the Genkin-Mednis procedure [22], which corresponds to an uncoupled Hartree-Fock scheme. The generalization to the coupled Hartree-Fock procedure has also been carried out first for the molecular hydrogen chains in order to assess the importance of the various parameters [23]. Very recently, we have investigated the relations between the nonsinglet Hartree-Fock instabilities and the polarizabilities for the hydrogen molecule, as well as the effect of applying an external electrical field on the Hartree-Fock instabilities of H_2 [24]. The molecular hydrogen model chains consist thus of ideal systems to investigate the effect of electron correlation on the longitudinal polarizability of increasingly large systems.

Section III gives thus the longitudinal polarizability results of these systems as a function of chain length and the atomic basis set. The choice of the basis set is very important and is influenced by the technique to be applied, as well as the property under investigation. In molecular systems, larger basis sets are necessary to reach basis set saturation in correlated calculations than in Hartree-Fock calculations. In other words, the basis set effects are significantly more important when electron correlation is included [25]. In one-dimensional extended systems, it is known from Hartree-Fock polarizability and hyperpolarizability calculations that the basis set quality is improved in the longitudinal direction because the deficiency of the basis set on any atom in one unit cell (or on one site) is compensated for by the atomic orbitals on neighboring unit cells (or sites) [6,10–12,26]. By using different extrapolation procedures, the asymptotic longitudinal polarizabilities per unit cell are computed. These asymptotic longitudinal polarizability results are then analyzed in order to define which atomic basis set one has to chose and up to what level of electron-electron interactions one should go to provide reliable estimates of the longitudinal polarizability of large systems. The accuracy of both the finite-field procedure and the extrapolation technique has been questioned. Since the Møller-Plesset treatment of electron correlation enables a decomposition of the energy in several terms characterized by their order and their class of substitutions, we have also investigated the importance of these various contributions to the longitudinal polarizability per unit cell of growing molecular hydrogen chain models.

II. METHODOLOGY

Nowadays, many theoretical techniques exist to compute the polarizability of molecular systems that do or do not include electron correlation [27–43]. Two classes of methods are distinguishable according to the quantities required to compute the polarizability. In the first class of techniques, one needs to know the field-perturbed wave functions and energies (or their derivatives with respect to that electrical field) to obtain the polarizability values [27–33], whereas, in the second class, the polarizabilities can be obtained directly without any knowledge of these field-perturbed wave functions [35–43].

Another classification key relies on the polarizability definition, which can be considered as the linear response of the dipole moment to an external electric field or as the second-order term in the perturbation expansion of the electronic energy with respect to that electric field. When the Hellmann-Feynman theorem [44] is satisfied, i.e., when dealing with procedures that are variational with respect to all the parameters [this is the case of the exact solution of the nonrelativistic electronic Schrödinger equation obtained by the full configuration-interaction (CI) technique and of the Hartree-Fock approximation, whereas the Møller-Plesset and the coupled-cluster techniques do not satisfy that theorem], both procedures are equivalent and one may write

$$\overleftrightarrow{\alpha}=-\left[\frac{\partial^2\mathcal{E}(\vec{E})}{\partial\vec{E}^2}\right]_{\vec{E}=0}=\left[\frac{\partial\vec{\mu}(\vec{E})}{\partial\vec{E}}\right]_{\vec{E}=0}. \tag{1}$$

In the first class of techniques, the evaluation of the linear response of the dipole moment or the quadratic response of the energy with respect to the external electric field is performed either analytically or numerically. Indeed, if no analytical procedure is available, the numerical finite-field (FF) technique can always be used. The FF technique consists of computing the dipole moment of a system under external electric fields of different amplitudes and considering a finite-difference formula [27]

$$\alpha_{ij}=\left[\frac{\partial\mu_i(E_j)}{\partial E_j}\right]_{\vec{E}=0}=\lim_{E_j\to0}\frac{\mu_i(E_j)-\mu_i(-E_j)}{2E_j}=\lim_{E_j\to0}\frac{\mu_i(E_j)}{E_j}, \tag{2}$$

where the last equality holds only for centrosymmetric compounds. In the alternative finite-difference technique, the central quantity is the field-dependent energy and in consequence, the polarizability is related to its second-order derivative

$$\alpha_{jj}=-\left[\frac{\partial^2\mathcal{E}(E_j)}{\partial E_j^2}\right]_{\vec{E}=0}=\lim_{E_j\to0}-\frac{\mathcal{E}(E_j)+\mathcal{E}(-E_j)-2\mathcal{E}(0)}{E_j^2}=\lim_{E_j\to0}2\frac{\mathcal{E}(0)-\mathcal{E}(E_j)}{E_j^2}. \tag{3}$$

Again, the last equality only concerns centrosymmetric systems. As stated above, expressions (2) and (3) provide different solutions when the Hellmann-Feynman theorem is not satisfied. Expression (3) is often used when dealing with techniques including electron correlation where the dipole moment (computed from the wave function) is not directly available. The Hartree-Fock (HF) FF procedure consists of the simplest level of application of the FF technique where the field-induced relaxation of the orbitals has been considered self-consistently. Then, electron correlation corrections can be included. In a size-consistent way, electron correlation can be examined in the framework of many-body perturbation theory by adopting the Møller-Plesset partitioning [16]. 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 [17]. In this work, in the coupled-cluster *Ansatz* all double excitations (CCD), all single and double excitations (CCSD), and all single and double excitations as well as a perturbational estimate of the connected triple excitations are accounted for (CCSDT). Many works have already been performed where the polarizability tensor has been obtained by numerical derivative of the energy obtained at these MP2, MP3, MP4, etc. [25,28–30], CCD, CCSD, CCSDT, etc. [30,31] levels. Due to the substantial amount of time required, such highly correlated calculations have been restricted to atoms or small molecules. The FF procedure could also be used in the CI framework. However, when the CI expansion is truncated (which is generally the case in all calculations on large systems), the CI treatment is not size consistent, i.e., it does not scale properly with the size of the system and, as a consequence, the CI-based methods should be avoided when dealing with increasingly large oligomers. This is not the case of the Møller-Plesset and the coupled-cluster treatments of electron correlation, which satisfy the size-consistency condition. Adopting an FF procedure allows the exploitation of theories and programs that have been developed and tuned for the usual correlation problem, the disadvantage of that being the need to carry out several calculations per polarizability calculation [see Eqs. (2) and (3)] and the numerical errors associated with the derivative procedure. This last point will be tackled later in this work.

At the Hartree-Fock level, the analytical technique is the coupled perturbed Hartree-Fock (CPHF) procedure [32]. Both HF FF and CPHF methods include field-induced electron reorganizational effects in a way that is fully consistent in terms of adjustments in the average two-electron interactions. Therefore, these techniques are said to be *coupled* Hartree-Fock (CHF) procedures. An analytical procedure based on the evaluation of pseudoenergy derivatives has been developed by Rice and Handy [33] in order to calculate the polarizability at the MP2 level.

In the second class of techniques one finds the procedures often referred to as summation over states (SOS) due to the form of the static polarizability expression [34]

$$\overleftrightarrow{\alpha}=2\sum_{n\neq0}\frac{|\langle\Psi_0|\vec{r}|\Psi_n\rangle|^2}{E_n-E_0}, \tag{4}$$

where the sum runs over all the excited states of the system, Ψ_0 and Ψ_n being the ground- and the excited-state wave functions associated with the energies E_0 and E_n, respectively; $\vec{r}$ is the dipole moment operator. A usual approximation to this exact expression is obtained by using as wave functions the Hartree-Fock-Slater determinants constructed from the Hartree-Fock occupied and unoccupied one-electron spin orbitals [35]. This is called the uncoupled Hartree-Fock (UCHF) technique because the field-induced electron reorganizational effects are not taken into account [36]. In fact, only field-induced one-electron effects are accounted for in the UCHF procedure. Improvements to this UCHF result are obtained by using CI wave functions including single, double, triple, etc., excitations [37]. Again, these CI 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. On the other hand, Eq. (4) includes information about the importance of the excited states in the polarizability value, which turns out to be an advantage in the design of new compounds for nonlinear optics applications [1].

Although not used in this work, we should mention the important class of methods based on the polarization propagator techniques [38], the linear-response theory [39], and the equation of motion coupled cluster [40] in which the electron correlation effects may also be included up to the desired level in electron-electron interaction. In these approaches, the electric response is also computed directly without any knowledge of the field-perturbed wave functions and energies. After some transformations, these polarizability estimates [38–40] can also be written in a SOS form. Recently, Sasagne, Aiga, and Itoh [41] presented a higher-order response theory scheme to evaluate the frequency-dependent polarizabilities and hyperpolarizabilities by means of the differentiation of quasienergy with respect to the strength of time-dependent external fields. Their procedure has been developed for single-exponential transformation *Ansätze* (HF and full CI) and for double-exponential transformation *Ansätze* [truncated CI and multiconfiguration self-consistent field (MCSCF)]. They derived also expressions based on quasienergy derivatives for computing the linear and the nonlinear responses in the Møller-Plesset treatment of the correlation energy [42] as well as in the coupled-cluster theory with Brueckner orbitals [43]. However, to our knowledge, no results have already been published from this powerful quasienergy derivative formalism.

In this work, the minimal STO-3G [45] and double-ζ (3)-21G [46] atomic basis sets have been chosen as well as the double-ζ plus polarization (6)-31G($*$)$*$ [47] and triple-ζ plus polarization (6)-311G($*$)$*$ [48] atomic basis sets. The parentheses in these basis set notations hold for the absence of core functions and core electrons for the hydrogen atom. The polarizability calculations have been performed at the MP2, MP3, MP4, CCD, CCSD, and CCSDT levels of approximation as well as at the coupled and the uncoupled Hartree-Fock levels. All the calculations reported in this work have been carried out by using GAUSSIAN92 [49] 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 [50] on the polarizability values obtained from the finite-field procedure based on Eq. (3). Lowering these thresholds is necessary to avoid any oscillatory behavior of the polarizability per unit cell values as chain grows. 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} [49]. The MP2 polarizability values are also evaluated analytically. In the other cases (MP3, MP4, CCD, CCSD, and CCSDT), a finite-field procedure has been adopted where, 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) have been employed. 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 [50]. Indeed, if the field amplitude is too large, the contaminations from the higher-order hyperpolarizabilities are increasing, whereas if the field amplitude is too small, the number of significant digits in the dipole or energy differences [Eqs. (2) and (3)] goes down. Romberg's procedure [51] is used to improve the finite-derivative technique. In this case where three field amplitudes (0.0, 0.0016, and 0.0032 a.u.) 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). This technique corresponds exactly to the one proposed by Bartlett and Purvis [29] and used by Sim *et al.* [52].

III. RESULTS AND DISCUSSION

The intermolecular (intramolecular) distances of the molecular hydrogen model chains have been chosen to be 3.0 a.u. (2.0 a.u.) (see Fig. 1) in order to present the polarizability exaltation feature described in the Introduction. The longitudinal polarizability results obtained with the different atomic basis sets and techniques are listed in Tables I–VIII.

To have access to the polarizability of the polymer, one has to consider the longitudinal polarizability per unit

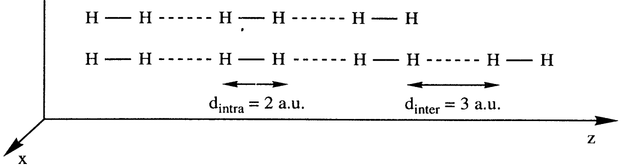

FIG. 1. Cartesian space representation of the molecular hydrogen chain models.

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

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	5.736	9.179	9.257	9.726
2	14.882	22.138	22.066	22.580
3	24.828	36.373	36.128	36.670
4	34.937	50.849	50.407	50.951
5	45.076	65.383	64.743	65.298
6	55.219	79.928	79.087	79.653
7	65.363	94.474	93.434	94.013
8	75.508	109.021	107.780	108.372
9	85.652	123.568	122.127	122.733
10	95.797	138.115	136.474	137.093
11	105.941	152.662	150.820	151.453
12	116.095	167.209	165.167	165.814

TABLE III. Longitudinal polarizability values of molecular hydrogen model chains as a function of the number of structural H_2 units (N) computed at the MP2 level of approximation by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*]. All the values are given in a.u. (1.0 a.u. of polarizability is equal to 1.6488×10^{-41} $C^2\,m^2J^{-1}=0.148\,18$ Å^3).

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	5.153	9.830	10.532	11.575
2	14.407	26.926	28.696	30.598
3	25.272	48.162	51.374	54.159
4	36.736	71.350	76.205	79.857
5	48.427	95.490	102.113	106.654
6	60.213	120.105	128.568	134.004
7	72.044	144.971	155.317	161.657
8	83.900	169.980	182.235	189.486
9	95.771	195.076	209.257	217.422
10	107.651	220.227	236.346	245.428
11	119.537	245.415	263.479	273.481
12	131.428	270.630	290.644	301.567

cell, which can be given by the longitudinal polarizability difference between two consecutive oligomers $\alpha_{zz}(N)-\alpha_{zz}(N-1)$. Such an expression possesses the advantage over the relative polarizability expression $\alpha_{zz}(N)/N$ of removing most of the chain-end effects. As the chain length increases, the longitudinal polarizability per unit cell increases and then saturates for longer chains. Under this saturation regime, the longitudinal polarizability evolves linearly with chain length. However, one should be cautious when stating that the evolution of the longitudinal polarizability per unit cell with chain length becomes linear for chains containing more than N unit cells since the behavior is never exactly linear and the increase continues, though at a much slower rate. This is thus a question of judgement, which is directly related to the accuracy that is required. The behavior of $\alpha_{zz}(N)-\alpha_{zz}(N-1)$ with chain length is depicted in Fig. 2 for the various techniques with the (3)-21G and (6)-311G(*)* atomic basis sets.

Since for the largest chains considered in this study the variation of $\alpha_{zz}(N)-\alpha_{zz}(N-1)$ is still larger than 10^{-2} a.u., one has to extrapolate in order to predict the polymeric results with a 5×10^{-3} a.u. accuracy. However, this is not the case of the UCHF values, which saturate much more rapidly as a consequence of the lack of any electron reorganizational effects that are governed by the long-

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

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	5.812	10.852	11.312	12.331
2	16.698	29.821	30.562	31.958
3	29.742	53.423	54.427	56.105
4	43.639	79.216	80.443	82.297
5	57.881	106.100	107.536	109.534
6	72.279	133.544	135.182	137.301
7	86.753	161.294	163.132	165.362
8	101.270	189.224	191.259	193.594
9	115.813	217.263	219.495	221.933
10	130.371	245.374	247.803	250.341
11	144.941	273.533	276.159	278.796
12	159.518	301.725	304.549	307.285
13	174.102	329.943	332.964	335.798
14	188.689	358.180	361.397	364.329
15	203.281	386.430	389.846	392.875
16	217.874	414.692	418.305	421.432
17	232.470	442.963	446.773	449.998
18	247.068	471.241	475.249	478.571

TABLE IV. Longitudinal polarizability values of molecular hydrogen model chains as a function of the number of structural H_2 units (N) computed at the MP3 level of approximation by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*]. All the values are given in a.u. (1.0 a.u. of polarizability is equal to 1.6488×10^{-41} $C^2\,m^2J^{-1}=0.148\,18$ Å^3).

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	4.691	9.144	10.120	11.228
2	12.782	24.833	27.533	29.707
3	22.027	44.008	49.093	52.439
4	31.642	64.748	72.601	77.158
5	41.378	86.219	97.073	102.891
6	51.158	108.038	122.027	129.129
7	60.957	130.035	147.238	155.644
8	70.765	152.131	172.595	182.317
9	80.580	174.285	198.041	209.087
10	90.398	196.477	223.545	235.920
11	100.219	218.693	249.085	262.796
12	110.043	240.928	274.654	289.702

TABLE V. Longitudinal polarizability values of molecular hydrogen model chains as a function of the number of structural H_2 units (N) computed at the MP4 level of approximation by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*]. All the values are given in a.u. (1.0 a.u. of polarizability is equal to 1.6488×10^{-41} $\mathrm{C^2\,m^2J^{-1}}=0.148\,18$ Å^3).

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	4.485	8.804	9.915	11.052
2	12.125	23.829	26.962	29.252
3	20.753	42.026	47.998	51.590
4	29.667	61.611	70.882	75.869
5	38.660	81.829	94.698	101.137
6	47.679	102.341	118.972	126.899
7	56.706	122.998	143.491	152.928
8	65.737	143.734	168.146	179.111
9	74.772	164.516	192.884	205.387
10	83.807	185.327	217.677	231.723
11	92.844	206.158	242.504	258.102
12	101.883	227.001	267.356	

range Coulombic interactions. These asymptotic values are obtained by extrapolating to infinite length the expression

$$\alpha_{zz}(N)-\alpha_{zz}(n-1)=a-be^{-cN}\ , \tag{5}$$

of which the parameters have been obtained by fitting the molecular results. The asymptotic polymeric values, given by a, are given at the top of Table IX. Five points have been used in these fittings. These points are associated with the longest chains because their longitudinal polarizability per unit cell value is closer to the asymptotic value than the smallest chains. The accuracy on the extrapolated values has been estimated by the fluctuation on the a value by comparison with the values associated with using the four largest oligomers in the fitting procedure.

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

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	4.230	8.382	9.690	10.867
2	11.253	22.512	26.262	28.640
3	18.997	39.284	46.438	50.181
4	26.882	57.086	68.221	73.415
5	34.779	75.307	90.769	97.485
6	42.667	93.702	113.688	121.966
7	50.548	112.175	136.803	146.669
8	58.424	130.687	160.028	171.499
9	66.297	149.220	183.319	196.407
10	74.170	167.767	206.652	221.367
11	82.040	186.322	230.015	246.359
12	89.910	204.886	253.396	271.373

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

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	4.433	8.619	9.756	10.886
2	12.092	23.316	26.427	28.649
3	20.816	40.981	46.756	50.186
4	29.877	59.897	68.730	73.421
5	39.049	79.370	91.491	97.497
6	48.264	99.102	114.641	121.989
7	57.500	118.963	137.996	147.705
8	66.746	138.897	161.467	171.550
9	75.998	158.872	185.010	196.475
10	85.255	178.875	208.597	221.452
11	94.515	198.898	232.218	246.462
12	103.777	218.933	255.860	

Since the Hartree-Fock results are much more easily accessible from the computational point of view, an alternative approach to get the extrapolated values within the correlated techniques consists of using the Hartree-Fock results as templates and of considering the evolution with chain length of the ratio α(with electron correlation)/α(coupled Hartree-Fock) [53]. Indeed, the CHF calculations can be performed much more easily for longer and longer chains, increasing therefore the accuracy on the extrapolated value. Fitting the function

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

to these ratios, where the different rates of saturation of the polarizabilities calculated at different levels of ap-

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

N	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
1	4.415	8.619	9.756	10.886
2	12.130	23.392	26.497	28.751
3	20.956	41.262	47.029	50.544
4	30.139	60.487	69.307	74.149
5	39.465	80.332	92.439	98.665
6	48.842	100.474	115.994	123.635
7	58.242	120.769	139.773	148.850
8	67.667	141.143	163.680	174.206
9	77.087	161.566	187.665	199.648
10	86.517	182.026	211.701	325.148
11	95.951	202.506	235.768	250.689
12	105.389	222.997	260.860	

proximation have been considered, provides the extrapolated polarizability values given in the middle of Table IX. The correlated asymptotic polarizability value is then given by

$$\alpha_{zz}(\text{correlation})=\alpha_{zz}(\text{CHF})a \; . \tag{7}$$

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

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

As depicted in Fig. 3 for the (6)-31G(*)* basis set and the CCD technique, this ratio converges faster than both the corresponding polarizabilities per unit cell. As a consequence of the sampling of the CHF results that incorporate larger chains, the extrapolated values using expressions (6) and (7) are larger than those obtained by the more commonly used fitting procedure (5). In addition, they are also of better quality. However, when the size of the oligomers becomes large enough, both approaches to get the asymptotic values have to furnish the same result and, as a consequence, their comparison provides an additional way of sampling the accuracy. As listed in Table IX, the agreement between the two procedures ranges from 1×10^{-2} to 6×10^{-2} a.u. It should be noted that several other forms for the fitting function have been presented and used to extrapolate the polarizability and other properties of polymeric chains to infinite chain limit [4,6–9]. For sufficiently large chain length, all these fittings should provide the same value, the accuracy being estimated by their comparison. This is, however, beyond the scope of this work, where we have chosen to restrain our procedure to Eqs. (5) and (6).

Taking care of the electron correlation clearly leads to a decrease of the longitudinal polarizability in the H_2 chains. This point can be rationalized by taking into account that, at the Hartree-Fock level, the electrons are forced to share more the same space as a result of the lack of electron correlation between electrons of different spin whereas, by including correlation between them, they are more localized and their associated polarizability decreases. Similar trends are observed for small molecules composed of carbon and hydrogen atoms, whereas the opposite is generally true when the molecule contains electronegative atoms such as nitrogen, oxygen, or fluorine [28,30,31].

Significant results are given at the bottom of Table IX and consist of the variation of the asymptotic polarizability per unit cell values obtained at different levels of approximation by increasing the basis set from (3)-21G to (6)-311G(*)* and from (6)-31G(*)* to (6)-311G(*)*. The asymptotic results obtained by following the second procedure have been retained for quantitative results of this comparison. At both the UCHF and the CHF levels, polarization functions and additional diffuse functions do not lead to a significant change of the longitudinal polarizability per unit cell (±1%). On the contrary, atomic basis set effects are much stronger when electron correlation is taken into account. The smaller effect is observed

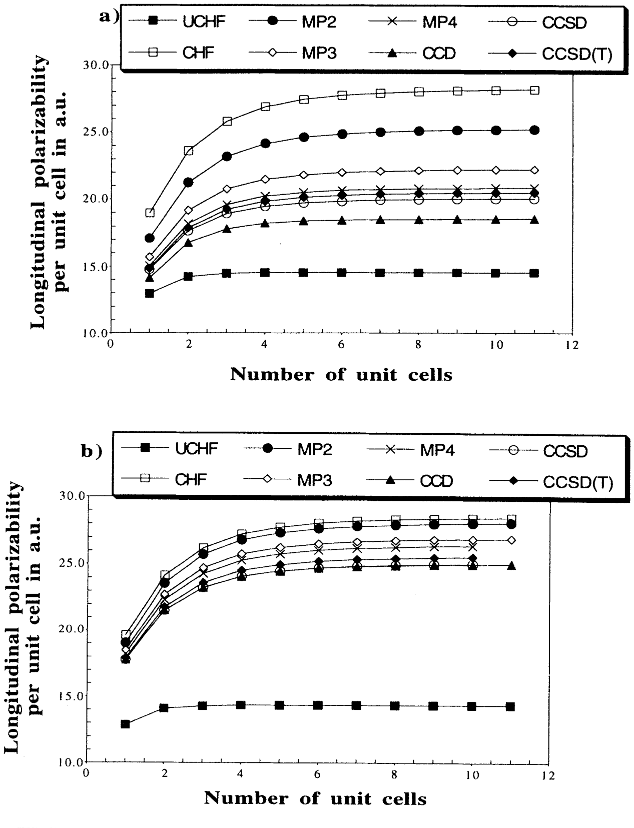

FIG. 2. Evolution with chain length of the longitudinal polarizability per unit cell $\alpha_{zz}(N)-\alpha_{zz}(N-1)$ of molecular hydrogen chain models computed at different levels of approximation. (a) (3)-21G, (b) (6)-311G(*)*.

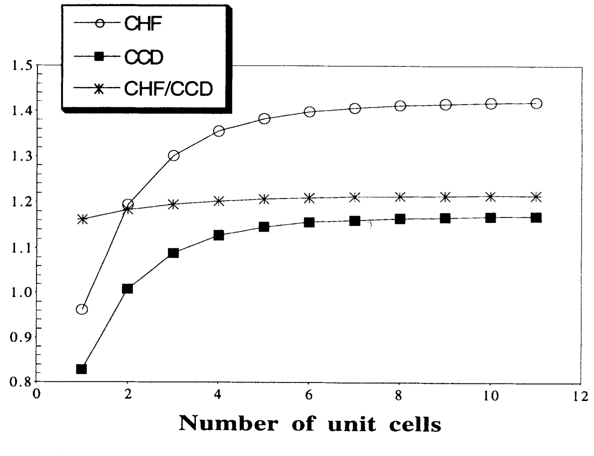

FIG. 3. Evolution with chain length of the CHF and the CCD longitudinal polarizability per unit cell of molecular hydrogen chain models and of their ratio. The (6)-31G(*) basis set has been used and the polarizability per unit cell values have been scaled by a factor of 0.05 to fit the graph.

TABLE IX. Asymptotic longitudinal polarizability per unit cell of molecular hydrogen model chains computed at various levels of approximation (UCHF, CHF, MP2, MP3, MP4, CCD, CCSD, and CCSDT) by using different atomic basis sets [STO-3G, (3)-21G, (6)-31G(*)*, and (6)-311G(*)*]. The top part tabulates the asymptotic values obtained after extrapolating the polarizability per unit cell obtained within the different techniques, whereas in the middle part, for the correlated results, the asymptotic values have been obtained after extrapolating the ratio with respect to the CHF results. See the text for a description of the extrapolation procedures. The last two rows list (in percent) the polarizability changes by going from smaller basis sets to larger basis sets. All the values are given in a.u.

Atomic basis set	UCHF	CHF	MP2	MP3	MP4	CCD	CCSD	CCSDT
STO-3G (I)	10.144±0.001	14.604±0.002	11.902±0.002	9.829±0.001	9.057±0.012	7.858±0.008	9.264±0.006	9.434±0.003
(3)-21G (II)	14.547±0.001	28.305±0.005	25.272±0.008	22.278±0.010	20.870±0.003	18.583±0.007	20.069±0.008	20.532±0.008
(6)-31G(*)* (III)	14.347±0.001	28.502±0.002	27.233±0.009	25.628±0.009	24.895±0.011	23.420±0.003	23.696±0.008	24.139±0.005
(6)-311G(*)* (IV)	14.361±0.001	28.602±0.004	28.160±0.010	26.973±0.010	26.458±0.014	25.048±0.005	25.071±0.004	25.631±0.020
STO-3G (ratio) (I)	10.144±0.001	14.604±0.002	11.911±0.002	9.839±0.002	9.050±0.002	7.881±0.003	9.278±0.003	9.452±0.002
(3)-21G (ratio) (II)	14.547±0.001	28.305±0.005	25.309±0.005	22.308±0.005	20.907±0.005	18.611±0.005	20.098±0.005	20.561±0.005
(6)-31G(*)* (ratio) (III)	14.347±0.001	28.502±0.002	27.270±0.003	25.663±0.003	24.943±0.002	23.460±0.002	23.726±0.002	24.176±0.002
(6)-311G(*)* (ratio)(IV)	14.361±0.001	28.602±0.004	28.198±0.004	27.010±0.004	26.508±0.004	25.105±0.004	25.128±0.004	25.666±0.004
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

at the less correlated level, the MP2 level. Including electron correlation results thus in a decrease of the polarizability values that is overestimated by using too small atomic basis sets. The difference between the CCD and the CCSD results disappears when the atomic basis set is augmented. This feature points out the predominant character of the multiple double excitations to describe the polarizability phenomena. Atomic basis sets larger than split-valence are thus required to correctly estimate the asymptotic polarizability per unit cell of large finite or infinite systems when electron correlation is included. For these large basis sets, it is, however, important to notice the weak effect with respect to the CHF results of including electron correlation: −1.4%, −5.6%, −7.3%, −12.2%, −12.1%, and −10.3% at the MP2, MP3, MP4, CCD, CCSD, and CCSDT levels of approximation, respectively, by using the (6)-311G(*)* basis set, whereas by using the (3)-21G basis set, the variations with respect to the CHF results are −10.6%, −21.2%, −26.1%, −34.2%, −29.0%, and −27.4% respectively. The CCSDT method including corrections from all single and double substitutions summed to all orders in electron-electron interactions and a perturbative treatment of the triple substitutions corresponds to the largest part of the exact electron correlation value among the techniques we have employed here. In addition, the corresponding polarizability values give very reliable results. The small polarizability variation by going from CCSDT to CCSD and to CCD shows that most of the electron correlation effects are reproduced by including the double substitutions summed to infinite order.

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

$$E(\mathrm{MP4})=E_{\mathrm{SCF}}+E_2^D+E_3^D+E_4^S+E_4^D+E_4^T+E_4^Q , \quad (9)$$

where E_4^Q contains the contribution from the disconnect-

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

Contribution	STO-3G	(3)-21G	(6)-31G(*)*	(6)-311G(*)*
α_{SCF}	14.604±0.002	28.305±0.005	28.502±0.002	28.602±0.004
$\alpha_2^D=\alpha_2$	−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

ed quadruple substitutions plus the renormalization. It is important to stress that each of these contributions is size extensive and therefore can be analyzed independently in the case of our incresingly large oligomeric models. An expression similar to (9) can be written for the polarizability,

$$\alpha(\text{MP4})=\alpha_{\text{CHF}}+\alpha_2^D+\alpha_3^D+\alpha_4^S+\alpha_4^D+\alpha_4^T+\alpha_4^Q \,. \quad (10)$$

Table X lists the different contributions to the asymptotic longitudinal polarizability per unit cell of the hydrogen chain models. The extrapolation have been performed by fitting the oligomeric results associated with the five largest chains to function (5). In the same way as for the total values, the accuracy has been sampled by removing one point in the fitting procedure.

The second-, third-, and global fourth-order contributions are all negative. Therefore, the more electron correlation, the smaller the asymptotic longitudinal polarizability per unit cell of the hydrogen chain models. Most of these electron correlation effects originate from the double substitutions. The third-order contribution is dominant if the atomic basis set is sufficiently extended (indeed, the contribution from the second-order double substitution is overestimated by using small basis sets). Single, triple, and quadruple substitutions contributions are very small. The single contribution is more important than the triple and quadruple contributions when using the minimal STO-3G atomic basis set, whereas with the (6)-31G(*) and (6)-311G(*)* atomic basis sets, the contribution from the triples is twice as much as that from the quadruples, the contribution from the singles being nearly one order of magnitude smaller than the triple contribution. The small contribution associated with the single substitutions reflects their inclusions in the coupled Hartree-Fock procedure. These three negative contributions associated with the second-, third-, and fourth-order corrections to the polarizability values differ from the works on small molecules [13,30,31] for which the α_3 and α_4 terms are generally of different sign and nearly compensate mutually. Moreover, the α_2 term is often positive as shown by the results of Sekino and Bartlett [31] (with the exception of the ethylene and nitrogen molecules) and of Sadlej [13] on small molecules. In addition, in these molecular calculations, α_2 is the leading term and α_3 often has a different sign. The calculations of Maroulis, and Archibong and Thakkar, on the CO molecule [30] corroborate this fact, whereas the results of Fowler and Dierksen on C_2H_2, C_2N_2, HC_3N, and C_4H_2 present a negative α_2 contribution [31]. In these triply bonded molecules, the α_4 contribution is important and it is difficult to rationalize the signs of α_3 and α_4.

It is also important to assess the evolution with chain length of the different contributions to the longitudinal polarizability per unit cell. With the exception of the $D2$ (within the notation, the letter refers to the class of substitutions, whereas the number refers to the order of the electron-electron interactions) contribution by using the (6)-311G(*)* atomic basis set, the amplitudes of the various contributions to the longitudinal polarizability per unit cell are all increasing with chain length. Since their evolution rates are different, the relative contribu-

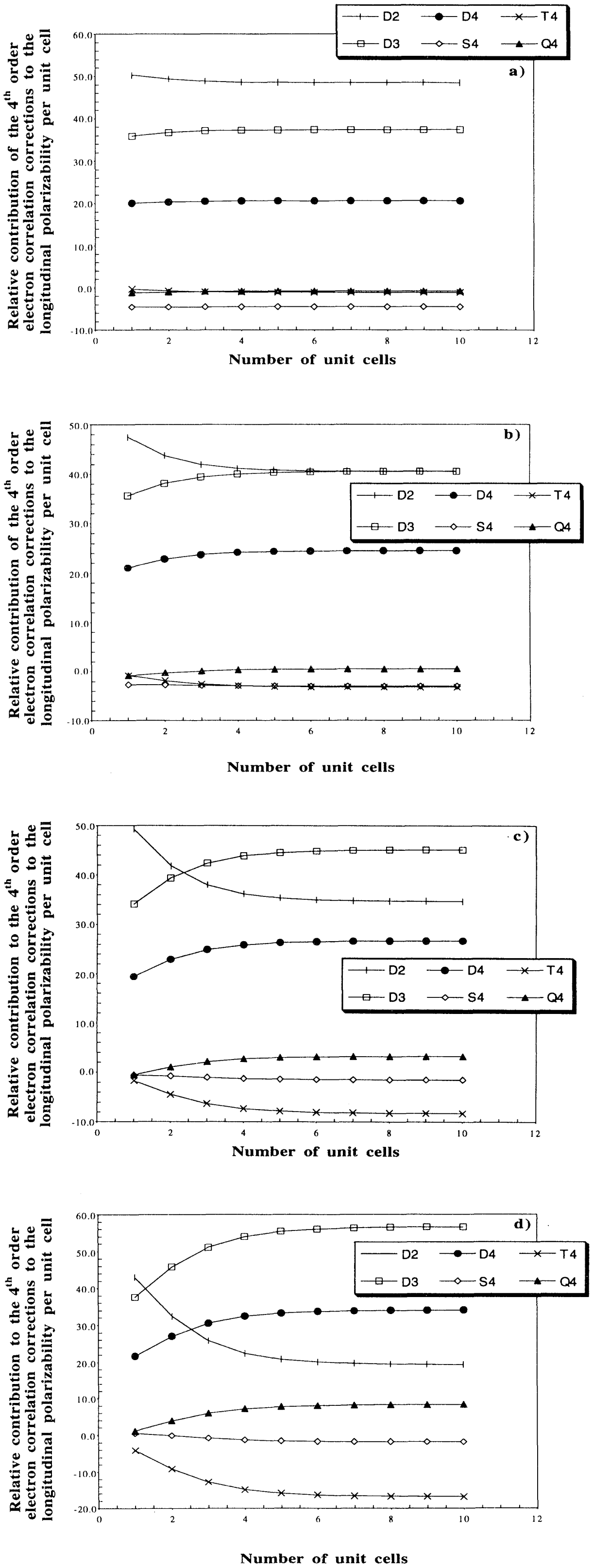

FIG. 4. Evolution with chain length of the relative contributions to the fourth-order electron correlation corrections to the longitudinal polarizability per unit cell. (a) STO-3G, (b) (3)-21G, (c) (6)-31G(*)*, (d) (6)-311G(*)*.

tions are more suitable for an analysis of their importance. The evolution with chain length of the different relative contributions to the fourth-order electron correlation corrections, given by the general expression

$$\%\alpha_I^X = \frac{\alpha_I^X}{\alpha_2^D + \alpha_3^D + \alpha_4^S + \alpha_4^D + \alpha_4^T + \alpha_4^Q} \times 100 , \qquad (11)$$

are reported in Fig. 4. These relative contributions can be grouped in two categories regarding their increasing or decreasing behavior with chain length. The STO-3G basis set results do not present any striking effects with chain length. $D2$ and $Q4$ have decreasing relative contributions when the chain length grows, while the opposite is true for the $D3$, $D4$, and $T4$ contributions and to a lesser extent for the $S4$ contribution. As a consequence, by using the (6)-31G(*)* and (6)-311G(*)* atomic basis sets, the second-order contribution is the largest for the smallest chains, while for chains containing more than three H_2 units, it becomes smaller than the third-order contribution with the (6)-31G(*)* atomic basis set and smaller than the third- and fourth-order double substitutions contributions with the (6)-311G(*)* atomic basis set. Using a too small atomic basis set, the second-order contribution is overestimated.

IV. SUMMARY, CONCLUSION, AND OUTLOOK

Different correlated techniques (MP2, MP3, MP4, CCD, CCSD, and CCSDT) have been used to investigate the effects of including electron correlation on the evaluation of the static asymptotic longitudinal polarizabilities per unit cell of molecular hydrogen chain models. Unlike uncoupled and coupled Hartree-Fock calculations for which a split-valence atomic basis set already provides suitable longitudinal polarizability estimates, the MP2, MP3, MP4, CCD, CCSD, and CCSDT techniques require at least additional polarization functions and triple-ζ type basis set to give suitable polarizability values. It has also 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.

The Møller-Plesset breakdown shows that the double substitutions present the largest electron correlation correction to the coupled Hartree-Fock asymptotic longitudinal polarizabilities per unit cell. Moreover, among these double substitution contributions, the third-order contribution is dominant if the atomic basis set is sufficiently extended. However, for chains containing less than three H_2 units, the second-order contribution is the most important: subsequently, it becomes smaller than the third-order contribution and eventually smaller than the fourth-order double substitutions contribution. Work is now in progress to investigate the variation of these electron correlation effects on the asymptotic longitudinal polarizabilities per unit cell as a function of bond-length alternation.

It should be stressed that these electron correlation effects will be emphasized if considering the frequency-dependent polarizability values. Indeed, electron correlation affects strongly the excitation energy values that correspond to the poles of the frequency-dependent polarizability.

ACKNOWLEDGMENTS

B.C. thanks the Belgian National Fund for Scientific Research for financial support. M.V. thanks the Human Capital and Mobility program (EICOC, European Initiative in Computational Chemistry). This work has benefited from the financial support of the Belgian National Interuniversity Research Program on "Sciences of Interfacial and Mesoscopic Structures" (PAI/IUAP No. P3-049). All calculations have been performed on the IBM RS6000 cluster of the Namur Scientific Computing Facility. The authors gratefully acknowledge the financial support of the FNRS-FRFC, the "Loterie Nationale" for the convention No. 9.4593.92, and the FNRS within the framework of the "Action d'Impulsion à la Recherche Fondamentale" of the Belgian Ministry of Science under the convention No. D.4511.93.

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