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Electron correlation effects on the static longitudinal second hyperpolarizability of polymeric chains. Møller–Plesset perturbation theory investigation of hydrogen model chains

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Ab initio calculations of the static longitudinal second hyperpolarizability of molecular hydrogen model chains have been performed 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 atomic basis set. Inclusion of electron correlation within the Møller–Plesset schemes limited to second (MP2), third (MP3), and fourth (MP4) order in electron–electron interactions leads to an increase of the longitudinal second hyperpolarizability per unit cell which is mainly due to the second-order correction provided that a sufficiently extended basis set is used. Indeed, whereas the basis set does not influence significantly the UCHF and CHF values, a too small basis set underestimates the positive second-order contribution, overestimates the negative third-order contribution and leads to a fourth-order contributions having an incorrect sign. This positive electron correlation correction for the second hyperpolarizability is opposite to the negative correction brought to the static longitudinal polarizability per unit cell for which the CHF level with a split-valence basis set provides reliable polarizability estimates. The present investigation points out that good estimates of the second hyperpolarizability are already obtained by using the MP2 procedure with a sufficiently extended basis set. © 1996 American Institute of Physics. [S0021-9606(96)01733-3]

I. INTRODUCTION

The inclusion of electron correlation effects in quantum chemical calculations of second hyperpolarizabilities, γ , of molecules affects strongly the estimated values. By adopting the Møller–Plesset partitioning in the framework of many-body perturbation theory (MBPT), Bartlett and Purvis¹ were the first to investigate these electron correlation effects on γ in the case of the hydrogen fluoride and water molecules. For hydrogen fluoride, at the coupled Hartree–Fock (CHF) level, the longitudinal second hyperpolarizability γ_L is equal to 280 a.u., whereas including electron correlation up to the second and third orders in electron–electron interactions leads to values of 390 and 330 a.u., respectively. Considering in a fourth-order treatment the contributions due to the singles, the doubles, and the quadruples [CHF+SDQ–MBPT(4)] gives a value of 390 a.u. In the case of the water molecule for the γ component parallel to the C_2 axis, corrections of 224, –126, and 92 a.u. for the second-, third-, and SDQ-fourth-order electron correlation contributions are added to the CHF value of 490 a.u., respectively and therefore, the CHF+SDQ–MBPT(4) γ_L is equal to 700 a.u. Following these original works, many other theoretical investigations have been carried out on the evaluation of the static and dynamic second hyperpolarizabilities in which electron correlation effects are included either within a Møller–Plesset scheme or within coupled cluster approaches or, also, by

using configuration interaction and multireference configuration interaction techniques. We refer to the review of Shelton and Rice² for a compilation of these second hyperpolarizability calculations of small molecules including electron correlation corrections.

Conjugated organic oligomers and polymers are candidate systems for nonlinear optics (NLO) applications due to their large hyperpolarizabilities, their short response times, their high laser damage thresholds, their easy processability as well as the numerous possibilities offered by the organic synthesis to tune their optical, mechanical and electrical properties. Due to electron delocalization along the backbone, the second hyperpolarizability of conjugated oligomers grows supralinearly with chain length.³ In other words, the longitudinal component of the second hyperpolarizability tensor per unit cell γ_L/N (where N is the number of unit cells) increases with chain length for the shortest chains, then saturates and finally becomes constant for the longest chains. The quantum chemical determination of such NLO properties, as well as their understanding which aims to lead to structure–property relationships and to quantum chemistry aided design of promising NLO materials is not an easy task.⁴ Indeed, on one hand, the computed NLO response depends strongly upon the atomic basis set used as well as the level of approximation, whereas on the other hand, the frequency dispersion,⁵ the vibrational contributions,⁶ and the effects of the environment^{7–8} are other phenomena which need to be taken into account. This paper is concerned with

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the evaluation of electron correlation effects and their relation to the extent of the atomic basis set.

Ab initio calculations of γ_L/N in increasingly large oligomers have been mainly restricted to prototype compounds such as polyacetylene,^{9–13} polyynes,^{14–16} polysilane,¹⁷ polydiacetylene,¹⁸ polybutatriene,¹⁸ and polypyrrole¹⁹ chains; larger unit cells and/or chemical substitutions of the main backbone being scarce and only investigated at empirical or semi-empirical levels. The effects of electron correlation on the NLO responses have been evaluated for polyacetylene,¹³ polyynes,¹⁶ and polypyrrole^{16,19} chains. However, due to the enormous computational requirements, unfortunately these electron correlation studies have been limited either to a small basis set, if different correlated levels are investigated, or to the simplest correlated level to address the effects related to the extent of the atomic basis set. The choice of a model system such as molecular hydrogen chains enables to overcome this difficulty and thus to perform γ_L/N calculations at different correlated levels by using a wide range of atomic basis sets. The present study goes thus beyond our initial studies of the electron correlation and basis set effects upon the linear polarizability per unit cell α_L/N of similar molecular hydrogen model chains.^{20,21}

It is striking to note that electron correlation has both direct and indirect effects on the γ values. Indeed, the determination of the geometrical parameters also depends strongly upon the level of the correlated treatment. This is particularly the case for the bond length alternation which describes the degree of conjugation or electron delocalization along the conjugated polymeric chain and, therefore, which substantially influences the hyperpolarizabilities.^{13,16} In this study, the electron correlation dependence of the geometrical parameters is left aside and we concentrate only on the electron correlation effects in the calculation of γ .

The next section details the theoretical and computational frameworks by positioning the techniques we use for determining γ , by describing and assessing the accuracy of the finite field procedure, and by discussing a procedure to analyze the electron correlation corrections according to the different classes of substitutions and different orders in the electron–electron interactions. Section III gives and analyzes the static longitudinal second hyperpolarizability values as a function of chain length, atomic basis set and level of approximation. The conclusions and outlooks are drawn in Sec. IV.

II. THEORETICAL AND COMPUTATIONAL FRAMEWORKS

A. The molecular hydrogen model chains

Increasingly large molecular hydrogen model chains are built by the addition of successive H_2 units oriented along the z axis which forms the longitudinal direction (Fig. 1). The intermolecular (intramolecular) distances of the molecular hydrogen model chains have been chosen to be 3.0 a.u. (2.0 a.u.) in order to exhibit the length dependence of γ_L described in the Introduction.

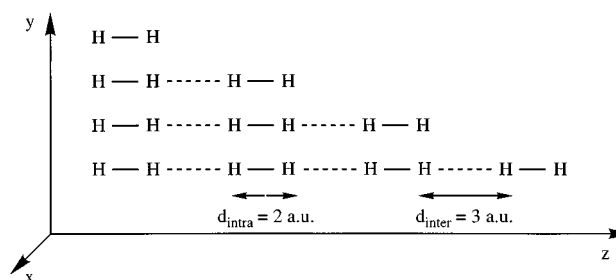


FIG. 1. Cartesian space representation of the molecular hydrogen chain models.

B. The static longitudinal second hyperpolarizability

The response of these centrosymmetric molecules to an homogeneous static electric field F_L directed along the longitudinal axis can be represented by the following two expansions

$$E(F_L) = E_0 - \frac{1}{2!} \alpha_L F_L^2 - \frac{1}{4!} \gamma_L F_L^4 - \dots, \quad (1)$$

$$\mu_L(F_L) = \alpha_L F_L + \frac{1}{3!} \gamma_L F_L^3 + \dots, \quad (2)$$

where E_0 is the energy of the molecule in the absence of the electric field, α_L is the longitudinal component of the electric dipole polarizability tensor, and γ_L is the longitudinal component of the electric dipole second hyperpolarizability tensor; the dipole moment and the first hyperpolarizability tensor being zero due to centrosymmetry. Both series have equivalent coefficients within variational approximation schemes [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 (HF) approximation whereas the Møller–Plesset perturbation technique does not satisfy this theorem] and, therefore, the second hyperpolarizability tensor reads

$$\gamma_L = - \left(\frac{\partial^4 E(F_L)}{\partial F_L^4} \right)_{F_L=0} = \left(\frac{\partial^3 \mu_L(F_L)}{\partial F_L^3} \right)_{F_L=0}. \quad (3)$$

This double equality leads to two ways to compute γ_L ; either as the negative of the fourth-order perturbation term or response of the energy with respect to the applied external electrical field or as the third-order response of the dipole moment to this field. Another classification of these methods to evaluate γ relies on the knowledge of the field-perturbed wave functions and energies (or their derivatives with respect to this field). So, the methods where the field derivatives of the energy or of the dipole moment is required form a first class, whereas the techniques based on the summation over

states (SOS) expression of γ coming from time-independent perturbation theory constitute a second class, together with propagator, response function and equation-of-motion techniques, the latter techniques requiring only field-free energy terms and dipole transition elements.

C. Hartree–Fock and Møller–Plesset methods

Starting from standard time-independent perturbation theory, γ_L is related to the fourth-order energy term by the SOS expression²²

$$\gamma_L = -24 \sum_{j \neq 0} \sum_{k \neq 0} \sum_{l \neq 0} \frac{\langle \Psi_0 | r_L | \Psi_j \rangle \langle \Psi_j | r_L | \Psi_k \rangle \langle \Psi_k | r_L | \Psi_l \rangle \langle \Psi_l | r_L | \Psi_0 \rangle}{(E_0 - E_j)(E_0 - E_k)(E_0 - E_l)} + 24 \sum_{k \neq 0} \frac{\langle \Psi_0 | r_L | \Psi_k \rangle \langle \Psi_k | r_L | \Psi_0 \rangle}{(E_0 - E_k)} \sum_{j \neq 0} \frac{\langle \Psi_0 | r_L | \Psi_j \rangle \langle \Psi_j | r_L | \Psi_0 \rangle}{(E_0 - E_j)^2} \quad (4)$$

where Ψ_0 is the ground state wave function of energy E_0 , Ψ_j is the j th excited state wave function of energy E_j , r_L is the longitudinal component of the electric dipole moment operator and $\langle \Psi_j | r_L | \Psi_k \rangle = \langle \Psi_j | r_L | \Psi_k \rangle - \langle \Psi_0 | r_L | \Psi_0 \rangle \delta_{jk}$. The uncoupled Hartree–Fock (UCHF) treatment is obtained by using Slater determinants formed from Hartree–Fock orbitals as approximate wave functions, while the associated energy is taken to be the sum of the energies of the orbitals in that determinant.⁹ At the UCHF level, the field-induced effects on the electron–electron interactions are not accounted for. Since the excitation energies are given by the orbital energy differences between the unoccupied and occupied one-electron levels, there is no interaction between the excited electron promoted to the unoccupied orbital and the hole left behind it. This leads to an overestimation of the excitation energies and generally an underestimation of γ . The HONDO 95.3 program²³ computes the UCHF γ values by following the algorithm of Fripiat *et al.*²⁴ that consists of the straightforward use of the molecular orbitals and energies calculated by the HF self-consistent-field procedure.

The coupled Hartree–Fock γ values are obtained analytically by iteratively solving the coupled-perturbed Hartree–Fock (CPHF) equations which provide the first and second field derivatives of the electron density matrix.²⁵ These are also computed by using the HONDO 95.3 program.²³ The CHF scheme includes the field-induced electron reorganizational effects in a way which 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 the field-induced one-electron effects are accounted for. In order to meet a 1.0 a.u. accuracy on the CHF γ_L values, the convergence thresholds on the wave-function derivatives have been tightened and set to 10^{-6} a.u. whereas the convergence criterion on the density matrix in the SCF procedure is set to 10^{-8} a.u.

Electron correlation has been examined in the MBPT framework by adopting the Møller–Plesset (MP) partitioning.²⁶ This leads thus to successive electron correlation corrections, namely MP2, MP3, ... which are consistent in electron–electron interactions through second, third, ... order,

respectively. These Møller–Plesset treatments of electron correlation are size consistent, i.e. the properties evolve correctly with the size of the chains. Since, to our knowledge, no analytical procedure yet exists to evaluate γ at the Møller–Plesset levels, we adopt a finite field procedure which is described in the following paragraph. When dealing with techniques which include electron correlation where the dipole moment computed from the wave function is not directly available, the finite field procedure is based on the field-dependent energies.

Considering the Møller–Plesset treatment of electron correlation, the total energy can be decomposed into several terms that are characterized by their order in electron–electron interactions (subscript) and the class of substitutions used in the intermediate states (superscript; S for single substitutions, D for double substitutions, ...). Hence, the energy up to fourth order in electron–electron interactions (E_{MP4}) can be rewritten,

$$E_{\text{MP4}} = E_{\text{HF}} + E_2^D + E_3^D + E_4^S + E_4^D + E_4^T + E_4^Q, \quad (5)$$

where E_4^Q contains the contribution from the disconnected quadruple substitutions and the renormalization. It is important to stress that each of these contributions is size extensive and, therefore, can be analyzed independently. A similar expression to (5) can be written for γ

$$\gamma_{\text{MP4}} = \gamma_{\text{CHF}} + \gamma_2^D + \gamma_3^D + \gamma_4^S + \gamma_4^D + \gamma_4^T + \gamma_4^Q. \quad (6)$$

In the analysis of the electron correlation effects, the CHF values are chosen as the reference. This can appear incorrect from a mathematical point of view because the field-free molecular orbitals and their associated energies (that directly enter in the UCHF polarizability expression) are the basis of the Møller–Plesset treatment. In addition, there is no doubt that the random phase approximation, which is equivalent to the CHF procedure, includes electron correlation. Therefore, one could say that the CHF procedure contains the lowest level of electron correlation. On the other hand, by analyzing the field-dependent Hartree–Fock equations, one sees that the CHF procedure merely represents a fully relaxed self-consistent field solution and, therefore, can be used as electron correlation free reference in our analysis.²⁷

In this work, the minimal STO-3G,²⁸ the double-zeta (3)-21G,²⁹ and (6)-31G,³⁰ and the triple-zeta (6)-311G³¹ atomic basis sets have been chosen, as well as double-zeta and triple-zeta basis sets augmented by one set of p -polarization functions, (6)-31G(*)³² and (6)-311G(*)³³ respectively. The parentheses in these basis set notations point out the absence of core functions since there are only two valence electrons in each H₂ molecule.

D. Finite field technique and Romberg's procedure

In order to calculate the electron-correlated γ_L , we have adopted the finite field (FF) procedure that consists of computing the total energy of a system under external electric fields of different amplitudes and considering a finite difference formula,³⁴

$$\begin{aligned}\gamma_L^{0,1} &= - \left(\frac{\partial^4 E(F_L)}{\partial F_L^4} \right)_{F_L=0} \\ &= \lim_{F_L \rightarrow 0} - \frac{8E(F_L) - 2E(2F_L) - 6E(0)}{F_L^4}.\end{aligned}\quad (7)$$

The simplest level of application of the FF technique consists of using the Hartree–Fock energies where the field-induced relaxation of the orbitals is considered self-consistently. This numerical scheme to compute the CHF polarizability is also equivalent to the analytical CPHF procedure. In the same way as for the Hartree–Fock energies, Eq. (7) can be used for the correlated energies. The advantage of adopting a FF procedure consists of the exploitation of theories and programs that have been developed and tuned for the inclusion of electron correlation energy corrections, whereas the disadvantages are the need to carry out several calculations per γ evaluation [see Eq. (7), at 0, F and $2F$ field amplitudes], the unbounded character of the dipole moment operator,³⁵ which can lead to unstable electronic configurations, as well as the potential numerical errors associated with the numerical derivative procedure.

The field amplitude has to be sufficiently small to satisfy the $F_L \rightarrow 0$ condition, as the contaminations from the higher-order hyperpolarizabilities increase as the even powers of the field amplitude. On the other hand, if the field amplitude is too small, the number of significant digits in the energy differences decreases. Optimal field amplitudes have thus been chosen while increased accuracy on the energy values has been imposed to meet the criteria for accuracy. In this way, we avoid any oscillatory behavior of the γ_L values per unit cell as the chain length increases, which would make the extrapolation procedure difficult. The Møller–Plesset energy calculations have been carried out by using the GAUSSIAN94³⁶ program by imposing tightened thresholds in the preceding SCF procedure, i.e., 10^{-14} a.u. for the requested convergence on the density matrix elements. The adopted field amplitudes are 0.0016, 0.0032, 0.0064, and 0.0128 a.u. (which correspond to 8.23, 16.46, 32.92, and 65.84×10^8 V/m, respectively). We note that the evaluation of γ_L requires much tighter thresholds and many more significant digits than the

evaluation of α_L due to the higher order of the numerical differentiation.

The higher-order hyperpolarizability contaminations have been successively removed by applying the Romberg's procedure.³⁷ Starting with second hyperpolarizability values $\gamma_L^{0,1}, \gamma_L^{0,2} \dots \gamma_L^{0,n}$ obtained with field amplitudes $F_L, 2F_L, \dots, 2^{n-1}F_L$, respectively, successive improvements to the second hyperpolarizability estimates can be calculated by the general iterative expression,

$$\gamma_L^{p,k} = \frac{4^p \gamma_L^{p-1,k} - \gamma_L^{p-1,k-1}}{4^p - 1}, \quad (8)$$

where p is the number of Romberg's iterations and k is related to the field amplitude. One Romberg iteration enables the removal of the $\epsilon_L F_L^6$ (ϵ_L is the fourth hyperpolarizability) contamination from the estimated γ_L value, and two and three iterations remove the successive contributions from the sixth and eighth hyperpolarizability contaminations, respectively. It is interesting to note that this procedure would be similar for noncentrosymmetric molecules provided that, in addition, calculations are performed with opposite field amplitudes. Test calculations on the Hartree–Fock finite field (in this way we may compare the results with the analytical CPHF values) γ values have been performed to address the choice of the field amplitudes that would meet the desired accuracy. Field amplitudes of 16×10^{-4} a.u., 32×10^{-4} a.u., 64×10^{-4} a.u., and 128×10^{-4} a.u. have been shown to be adequate to meet at least a 10 a.u. accuracy on the γ_L value which is obtained after two Romberg iterations; the remaining error being due to higher-order contaminations. On the other hand, larger field amplitudes (256×10^{-4} a.u. or 512×10^{-4} a.u.) lead to unstable electronic structures whereas smaller field amplitudes (4×10^{-4} a.u. or 8×10^{-4} a.u.) give rise in some cases to 100–500 a.u. fluctuations with respect to the CPHF results; showing thus the lack of significant digits.

E. Extrapolation procedure

In order to determine the asymptotic γ_L per unit cell, one considers the evolution of the variation of the γ_L between consecutive oligomers, $\Delta \gamma_L(N) = \gamma_L(N) - \gamma_L(N-1)$, as a function of chain length. Such a formula has the advantage of reducing the chain-end effects. Since for the largest chains the variation of $\Delta \gamma_L(N)$ is still significant, it is necessary to extrapolate in order to predict the polymeric result. The extrapolated asymptotic $\Delta \gamma_L(N)$ value is obtained by fitting the parameters of the following equation

$$\Delta \gamma_L(N) = a - b e^{-cN}, \quad (9)$$

to the molecular results, the asymptotic polymeric value 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. Since, due to computational resource limitations, the CHF calculations

can be carried out on larger oligomeric chains than the Møller–Plesset calculations, the extrapolated CHF values are more accurate than the corresponding extrapolated values including electron correlation. However, improved accuracy can be obtained for the correlated results by performing the extrapolation on the ratio $\Delta\gamma$ (with electron correlation)/ $\Delta\gamma$ (coupled Hartree–Fock) which converges faster than both of its components. Then, the extrapolated values including electron correlation are obtained after fitting the function

$$\frac{\Delta\gamma_L^{\text{MP}}(N)}{\Delta\gamma_L^{\text{CHF}}(N)} = \frac{a - be^{-cN}}{1 - de^{-fN}}, \quad (10)$$

to these ratios where the different rates of saturation of the $\Delta\gamma_L$ calculated at different levels of approximation have been considered. The correlation corrected asymptotic $\Delta\gamma_L$ values is then given by

$$\Delta\gamma_L(\text{MP}) = \Delta\gamma_L(\text{CHF}) * a. \quad (11)$$

Eight points have been used in these fittings. The accuracy on a is given by the variation on a obtained when restricting the oligomeric results to the seven longest chains whereas the uncertainty on the MP $\Delta\gamma_L$ 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,

$$\% \Delta\gamma_L(\text{MP}) = \sqrt{(\% \Delta\gamma_L(\text{CHF}))^2 + (\% a)^2}. \quad (12)$$

Many other forms of fitting functions (power series in $1/N$,^{10,12,18} Padé approximants³⁸) have been presented and used to extrapolate these hyperpolarizabilities but none of these fitting functions has presented an advantage; all of them having to give the same asymptotic value for a number of unit cells tending toward infinity. Nevertheless, an elegant and more systematic procedure which defines a stability criteria has been developed by Kirtman *et al.*¹² Since this is beyond the scope of this work, we have employed Eqs. (9)–(12) to get the asymptotic γ_L per unit cell values though the

comparison of these extrapolation procedures would obviously determine more accurately the asymptotic value and its range of uncertainty.

III. RESULTS AND DISCUSSION

Tables I and II list the UCHF and CHF longitudinal second hyperpolarizabilities of the increasingly large hydrogen model chains containing up to 30 hydrogen atoms with different atomic basis set and Tables III–V give the MP2, MP3, and MP4 results for chains as large as $[(\text{H}_2)_{10}]$. Figure 2 displays the evolution with chain length of $\Delta\gamma_L(N)$ as a function of the level of approximation for the different basis sets. In addition to the extrapolated $\Delta\gamma_L$ obtained by following the procedure previously described, Table VI gives also the relative electron–correlation percentage correction with respect to the CHF values as well as the percentage $\Delta\gamma_L(\infty)$ variation upon basis set extension.

For all the basis sets used, the UCHF $\Delta\gamma_L$ are much smaller and saturate more rapidly with chain length than the CHF and correlated $\Delta\gamma_L$. Similar features have already been shown for the $\Delta\alpha_L$ of hydrogen model chains^{20–21} and polyacetylene chains³⁹ and are due to the lack of electron reorganizational effects that are governed by the long-range Coulombic interactions. However, in both the UCHF and CHF approaches, the increasing order of the extrapolated $\Delta\gamma_L$ values is the same, i.e., (6)-311G > (6)-31G > (6)-311G(*) > (3)-21G > (6)-31G(*) > STO-3G; indicating that the CHF trends are generally reproduced at the UCHF level of approximation. At the UCHF and CHF levels, the addition of one set of p -polarization functions (p_x , p_y , and p_z) leads to a small (3%) decrease of $\Delta\gamma_L(\infty)$. With the exception of the minimal STO-3G basis set which strongly underestimates the γ_L values, all the basis sets considered here provide similar CHF $\Delta\gamma_L(\infty)$ values to within 5%, indicating thus that a split-valence basis set is already sufficient for estimating γ_L at the CHF level. Similar conclusions have been drawn by Hurst *et al.*¹⁰ for the γ_L of polyacetylene chains. In addition, the reliability of a split-valence

TABLE I. UCHF longitudinal second hyperpolarizability values (in a.u.) of molecular hydrogen model chains computed by using different atomic basis sets (1.0 a.u. of second hyperpolarizability = 5.0367×10^{-40} esu = $6.2354 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$).

	STO-3G	(3)-21G	(6)-31G	(6)-311G	(6)-31G(*)*	(6)-311G(*)*
1	−111.2	−339.5	−365.1	−219.0	−281.0	−136.6
2	799.2	2054.8	2266.7	3300.1	2343.8	3490.5
3	3209.3	8226.8	8808.9	10 745.2	8699.1	10 671.7
4	6566.9	16 853.7	17 735.1	20 086.0	17 359.9	19 773.7
5	10 321.5	26 662.5	27 871.2	30 754.4	27 144.0	30 034.1
6	14 206.4	36 888.9	38 412.4	41 650.2	37 302.8	40 535.3
7	18 127.4	47 250.0	49 088.1	52 732.5	47 584.6	51 191.3
8	22 057.2	57 647.6	59 798.9	53 819.2	57 897.8	61 856.6
9	25 989.0	68 054.4	70 519.2	74 925.0	68 219.0	72 536.9
10	29 921.2	78 463.2	81 241.4	86 029.0	78 541.6	83 216.1
11	33 853.4	88 872.3	91 963.9	97 134.8	88 864.4	93 896.6
12	37 785.6	99 281.4	102 686.4	108 240.3	99 187.0	104 576.8
13	41 717.8	109 690.4	113 408.8	119 346.0	109 509.5	115 257.1
14	45 649.9	120 099.3	124 131.1	130 451.6	119 832.0	125 937.3
15	49 582.1	130 508.2	134 853.4	141 557.3	130 154.4	136 617.5

TABLE II. CHF longitudinal second hyperpolarizability values (in a.u.) of molecular hydrogen model chains computed by using different atomic basis sets.

	STO-3G	(3)-21G	(6)-31G	(6)-311G	(6)-31G(*)*	(6)-311G(*)*
1	-65.0	-374.9	-432.5	-221.0	-423.6	-250.5
2	1563.5	3781.2	4235.7	7191.8	4075.9	7162.6
3	6842.1	18 878.3	20 334.4	26 275.1	19 561.8	25 699.1
4	15 523.1	46 340.5	48 986.1	57 333.1	47 171.5	55 932.4
5	26 380.7	83 687.6	87 629.9	98 153.0	84 425.3	95 534.5
6	38 419.8	127 646.8	132 902.3	145 187.6	128 086.6	141 181.0
7	51 072.7	175 755.9	182 345.5	196 281.6	175 773.8	190 738.4
8	64 052.3	226 427.6	234 362.9	249 821.1	225 947.7	242 672.8
9	77 215.5	278 703.6	287 996.0	304 930.7	277 681.9	296 127.5
10	90 488.7	332 009.9	342 668.6	361 043.0	330 420.3	350 557.3
11	103 831.9	385 998.2	398 030.9	417 827.6	383 824.9	405 640.4
12	117 222.1	440 452.3	453 865.4	475 072.9	437 685.5	461 171.8
13	130 645.2	495 234.2	510 032.9	532 644.9	491 867.7	517 021.1
14	144 092.2	550 253.7	566 442.0	590 454.6	546 283.2	573 102.0
15	157 557.1	605 449.6	623 031.1	648 442.0	600 872.3	629 355.8

basis set to offer adequate UCHF and CHF $\Delta\alpha_L$ values for model or prototype oligomeric and polymeric chains^{10,20,21,39,40} has also been demonstrated many times.

With the exception of the STO-3G calculations, the global effect of including electron correlation is an increase of γ_L and $\Delta\gamma_L$ which contrasts with the decrease of α_L and $\Delta\alpha_L$.^{20,21} For sufficiently extended basis sets, this global increase results from positive second- and fourth-order contributions and a negative third-order part. From Fig. 2, one sees that for the largest basis sets the MP3 and MP4 curves tend toward the MP2 curve which stands 20%–30% above the CHF curve. This phenomenon is different than for $\Delta\alpha_L$ where the MP2, MP3, and MP4 curves tend toward the CHF curve on enlarging the basis set. Indeed, at second order in the Møller–Plesset scheme the inclusion of electron correlation leads to an increase of $\Delta\gamma_L$ with respect to the CHF values; this increase being the largest for the most extended basis sets. By going further in the Møller–Plesset expansion, we observe that the third-order contribution is negative and therefore decreases the electron correlation correction to the CHF values. However, it is striking to note that the amplitude of this negative contribution decreases for the most extended basis sets. Then, the fourth-order correction is initially negative for the double- and triple-zeta basis sets but becomes positive when p -polarization functions are in-

cluded. Consequently, whereas the MP4 and CHF $\Delta\gamma_L^{(\infty)}$ values are close to each others with the (3)-21G, (6)-31G, and (6)-311G atomic basis sets, the MP4 values are 19.4% and 31.6% larger than the CHF values for the (6)-31G(*)* and (6)-311G(*)* atomic basis sets, respectively. In addition, the $\Delta\gamma_L^{(\infty)}$ variations by going from the MP2 to the MP4 levels are +14.0%, +19.7%, +17.4%, +9.3%, and +3.9% for the (3)-21G, (6)-31G, (6)-311G, (6)-31G(*)*, and (6)-311G(*)* atomic basis sets, respectively.

These γ_L increases upon inclusion of electron correlation are consistent with many other works performed on small- or medium-size molecules. By going from the CHF to the MP2 approximation, Perrin *et al.*⁴¹ calculated a 34% increase for the average γ of benzene, the γ_L of paranitroaniline⁴² increases by one hundred of percent, Hammond and Rice⁴³ found a 20% increase for HCl, and from the investigation of Sekino and Bartlett⁴⁴ on CO₂, N₂, H₂, C₂H₄, CO, HF, H₂O, NH₃, and H₂S, the average increase is around 40%–50%. It is striking to note that in the pioneering works of Bartlett and Purvis¹ on HF and H₂O, one already finds that the second-order contribution is the largest and positive, the third-order contribution is negative whereas the fourth-order contribution without the triple contribution is positive. [In a more recent work, the missing γ_4^T contribution has been calculated for HF by Sekino and Bartlett.⁴⁵ The value for γ_4^T of 50 a.u.

TABLE III. MP2 longitudinal second hyperpolarizability values (in a.u.) of molecular hydrogen model chains computed by using different atomic basis sets.

	STO-3G	(3)-21G	(6)-31G	(6)-311G	(6)-31G(*)*	(6)-311G(*)*
1	-4	-134	-167	73	-250	-79
2	1703	5162	5700	8959	5249	8471
3	6640	23 061	24 857	32 030	23 982	31 213
4	14 373	55 448	58 891	69 856	58 105	69 794
5	23 800	99 669	105 082	119 871	105 027	121 621
6	34 093	151 857	159 405	177 751	160 669	182 309
7	44 808	208 988	218 798	240 716	221 810	248 735
8	55 734	269 111	281 264	306 711	286 330	318 664
9	66 771	331 072	345 628	374 633	352 951	390 834
10	77 874	394 220	411 235	443 880	420 944	464 531

TABLE IV. MP3 longitudinal second hyperpolarizability values (in a.u.) of molecular hydrogen model chains computed by using different atomic basis sets.

	STO-3G	(3)-21G	(6)-31G	(6)-311G	(6)-31G(*)*	(6)-311G(*)*
1	61	112	107	387	-104	53
2	1679	5826	6384	9547	5557	8636
3	5772	23 374	25 209	32 170	23 853	30 925
4	11 685	53 723	57 308	68 109	56 452	68 257
5	18 528	94 115	99 857	114 636	100 779	118 023
6	25 763	141 047	149 194	167 805	153 022	176 075
7	33 147	191 908	202 643	225 164	210 222	239 458
8	40 588	245 072	258 516	284 963	270 406	306 085
9	48 051	299 612	315 850	346 284	332 452	374 771
10	55 524	355 024	374 125	408 648	395 699	444 855

maintains the fourth-order contribution positive and leads to a γ_{MP4} of 440 a.u.] Moreover the numerous and systematic studies on the prediction of second hyperpolarizability values of molecules by including electron correlation with a wide range of extended basis sets performed by Thakkar, Maroulis, and their co-workers show that the second-order contribution is positive and constitutes in most cases (C_2H_2 ,⁴⁶ C_4H_2 ,⁴⁷ C_2H_4 ,⁴⁸ Cl_2 ,⁴⁹ Br_2 ,⁴⁹ and CH_4 ⁵⁰) the major part; the only exception being O_3 ,⁵¹ where the negative fourth-order contribution is the largest. In all these studies,⁴⁶⁻⁵¹ the third-order contribution is negative and sometimes counterbalanced by a positive fourth-order correction.⁴⁹⁻⁵⁰

It is more striking to compare our results with these obtained on large oligomeric chains. Toto *et al.*¹³ have studied increasingly large polyacetylene chains ranging from C_2H_4 to $\text{C}_{24}\text{H}_{26}$ by using the 6-31G basis set, have shown that the MP2 γ_L values are nearly twice as large as the CHF ones whereas including electron correlation up to the fourth order decreases the MP2 γ_L by 4%–8%. They have also determined the asymptotic MP2/CHF and MP4/MP2 ratios of $\Delta\gamma_L$ which are tending to 1.9 and 0.92, respectively. By including the effects of electron correlation on the geometrical structure, the bond length alternation of infinite polyacetylene decreases from 0.112 to 0.085 Å, then, the field-induced electron delocalization is more favored and, the MP2/CHF ratio increases to 2.84 for the longest polyacetylene chain ($\text{C}_{24}\text{H}_{26}$). In the case of polyene chains, by considering the electron correlation effects on both the calculations of the geometry and the longitudinal second hyperpolarizability,

the extrapolated MP2/CHF ratio has been computed to be 8.0 whereas it is 1.9 when only taking into account the effects on the geometry.¹⁶ For comparison with polyacetylene, their bond length alternation considered for the increasingly large polyene chains decreases from 0.165 to 0.104 Å when passing from the HF to the MP2 treatment. For polypyrrole^{16,19} the global effect of electron correlation gives a MP2/CHF ratio for γ_L equal to 2.2 for the polymeric limit while it decreases to 1.4 when using the same geometry in both the correlated and uncorrelated calculations. In the case of polypyrrole, the bond length alternation decrease is of the same order (0.029 Å) as for polyacetylene. Consequently, putting aside the effects on the geometry, the inclusion of electron correlation at the MP2 level by using a 6-31G atomic basis set gives rise to increases of 90%, 420% (we have assumed that the multiplication of the electron correlation effects on the geometry and on the computed γ provides the global electron correlation correction) and 40% for polyacetylene, polyene, and polypyrrole, respectively; showing thus the great impact of the chemical nature of the chain and suggesting further investigations on hydrogen model chains of different bond length alternation.

It turns out from these calculations on these molecular hydrogen model chains that the MP2 technique with a large basis set [(6)-311G(*)] is a good procedure to provide suitable $\Delta\gamma_L(\infty)$ estimates. On the other hand, MP4 calculations with a split-valence basis set are not really effective. This efficiency of the MP2 approach to tackle the electron correlation correction to γ was already suggested by Sekino and

TABLE V. MP4 longitudinal second hyperpolarizability values (in a.u.) of molecular hydrogen model chains computed by using different atomic basis sets.

	STO-3G	(3)-21G	(6)-31G	(6)-311G	(6)-31G(*)*	(6)-311G(*)*
1	92	243	254	564	-27	125
2	1649	6041	6615	9742	5718	8784
3	5354	23 178	25 063	31 992	24 013	31 277
4	10 491	52 327	56 067	67 040	56 525	69 077
5	16 253	90 792	96 866	112 158	100 769	119 635
6	22 213	135 272	143 990	163 586	152 988	178 785
7	28 214	183 320	194 908	218 955	210 197	243 474
8	34 209	233 426	248 032	276 601	270 433	311 533
9	40 190	284 736	302 464	335 563	332 524	381 728
10	46 161	336 802	357 736	395 699	395 821	453 416

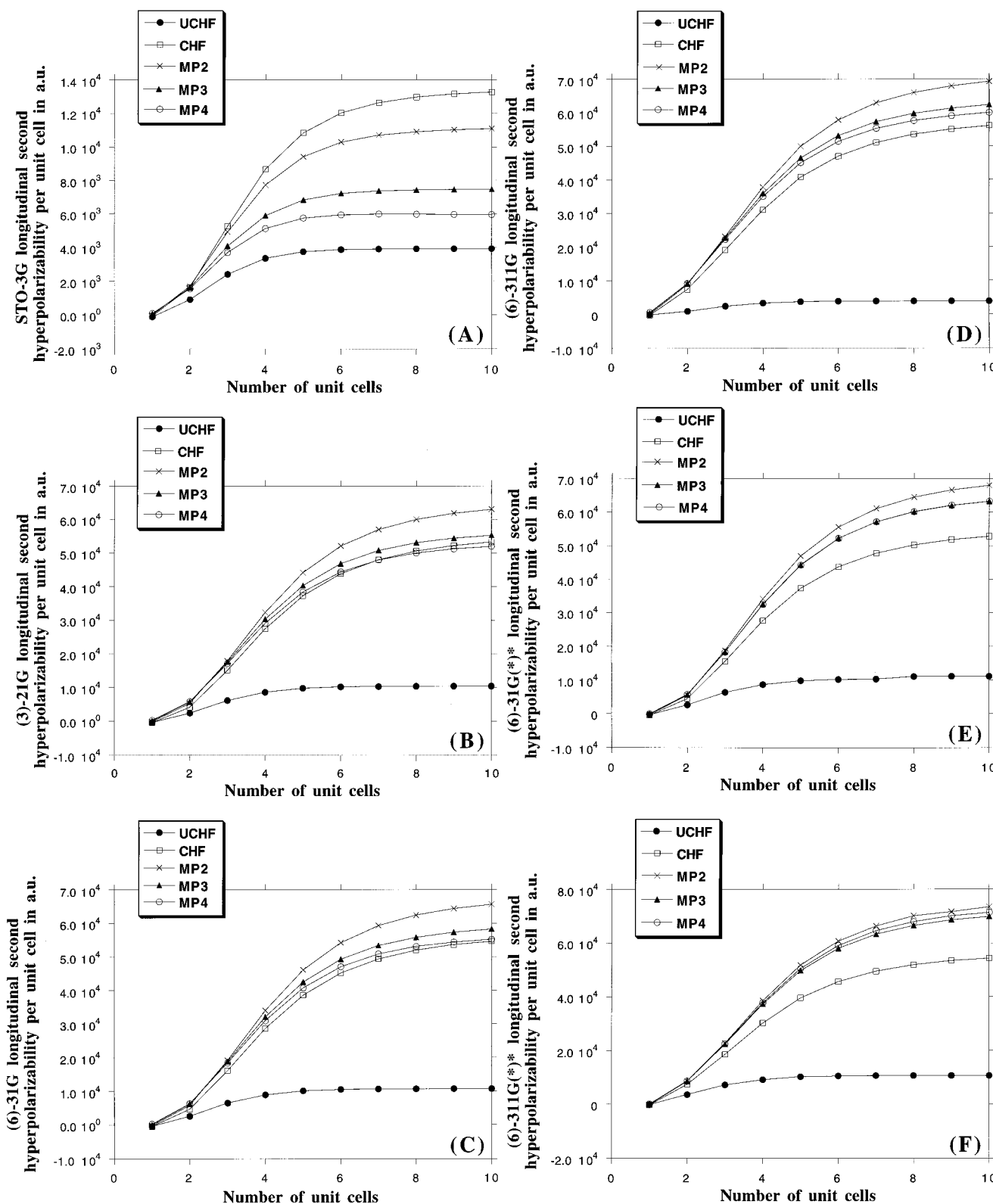


FIG. 2. Evolution with chain length of the static longitudinal second hyperpolarizability per unit cell $\Delta\gamma_L(N) = \gamma_L(N) - \gamma_L(N-1)$ in a.u. of molecular hydrogen model chains computed at different levels approximation by using different basis sets; (A) STO-3G, (B) (3)-21G, (C) (6)-31G, (D) (6)-311G, (E) (6)-31G(*), and (F) (6)-311G(*)

TABLE VI. Asymptotic γ_L per unit cell of molecular hydrogen model chains computed at different levels of approximation by using various atomic basis sets. The values given in italics below each extrapolated γ_L value correspond to the relative percentage correction with respect to the corresponding CHF values obtained with the same basis set. The last part of the table gives in percent the asymptotic γ_L per unit cell changes by going from smaller to larger atomic basis sets. All the γ_L values are given in a.u.

	UCHF	CHF	MP2	MP3	MP4
STO-3G	3932	13 515±6	11 258±5	7524±4	5980±9
(I)	<i>-70.9</i>		<i>-16.7</i>	<i>-44.3</i>	<i>-55.8</i>
(3)-21G	10 409	55 674±40	65 583±51	57 170±49	53 547±51
(II)	<i>-81.3</i>		<i>+17.8</i>	<i>+2.7</i>	<i>-3.8</i>
(6)-31G	10 722	57 080±43	68 092±52	60 135±52	56 836±49
(III)	<i>-81.2</i>		<i>+19.3</i>	<i>+5.4</i>	<i>-0.4</i>
(6)-311G	11 106	58 468±12	71 054±23	64 338±37	61 868±13
(IV)	<i>-81.0</i>		<i>+23.2</i>	<i>+10.0</i>	<i>+5.8</i>
(6)-31G(*)*	10 322	55 063±39	70 891±52	65 729±59	65 766±108
(V)	<i>-81.3</i>		<i>+28.7</i>	<i>+19.4</i>	<i>+19.4</i>
(6)-311G(*)*	10 680	56 732±37	76 845±50	73 002±49	74 683±54
(VI)	<i>-81.2</i>		<i>+35.5</i>	<i>+28.7</i>	<i>+31.6</i>
(I)→IV	+3.6	+2.5	+4.3	+7.0	+8.9
(II)→VI	+3.5	+3.0	+8.4	+11.1	+13.6
(III)→V	-3.7	-3.5	+4.1	+9.3	+15.7
(IV)→VI	-3.8	-3.0	+8.2	+13.5	+20.7

Bartlett⁴⁴ although these authors warned that this MP2 approach might be insufficient for systems with large electron delocalization.

As shown at the bottom of Table VI, the atomic basis set effects are small for the UCHF and CHF levels but increase more and more with the rate of inclusion of electron correlation. Moreover, at the MP3 and MP4 levels, these atomic basis set effects are larger on $\Delta\gamma_L(\infty)$ than on $\Delta\alpha_L(\infty)$.^{20,21} Indeed, in going from the (3)-21G to the (6)-311G(*)* basis set, $\Delta\alpha_L(\infty)$ increases by 11.4%, 21.1%, and 26.8% at the MP2, MP3, and MP4 levels, respectively whereas $\Delta\gamma_L(\infty)$ increases by 17.2%, 27.7%, and 39.5%. The addition of one set of *p*-polarization functions has a greater effect on $\Delta\gamma_L$ than the passage from a double- to a triple-zeta basis set. The results associated with the monomer H₂ and, to a lesser extent, the dimer present different features than those associated with longer chains. Indeed, for the small systems, both the atomic basis set and the method more strongly influence γ_L which can also change of sign [even if we do not take into account the UCHF technique and the minimal STO-3G results which underestimate the $\Delta\gamma_L(\infty)$ values]. This shows again that for small molecules, γ is very difficult to estimate^{43,48,50,52–54} and often requires the use of both diffuse and higher angular momentum polarization functions. On the

other hand, for large molecules the tensor component associated with extended directions (for instance the longitudinal direction of oligomeric chains) is less subject to these basis set effects. This enhancement of the quality of the basis sets has been first mentioned by Hurst *et al.*¹⁰ for polyacetylene chains.

The analysis of the Møller–Plesset contributions to $\Delta\gamma_L$ in terms of the type of substitutions and the order of the electron–electron interactions is shown as a function of chain length in Fig. 3 for different basis sets. Table VII lists the asymptotic values of these contributions that have been determined by using Eq. (9) in the extrapolation procedure. These results show again the major and positive $\Delta\gamma_2^D$ contribution and the negative $\Delta\gamma_3^S$ part but enable to see that $\Delta\gamma_4^D$ and $\Delta\gamma_4^O$ are always negative, $\Delta\gamma_4^T$ is always positive whereas $\Delta\gamma_4^S$ is positive for the most extended basis sets but negative for the smallest basis sets. This change of sign of $\Delta\gamma_4^S$ upon basis set extension as well as the decrease (increase) of the amplitude of $\Delta\gamma_4^D$ ($\Delta\gamma_4^T$) explains the sign change of the global fourth-order correction to $\Delta\gamma_L$. By focusing on the (6)-311G(*)* results, we remark that many similarities between the $\Delta\gamma_L$ and $\Delta\alpha_L$: the *D3*, *D4*, and *Q4* contributions are negative whereas the *S4* and *T4* contributions are positive in both cases. On the other hand, the *D2*

TABLE VII. Contributions of the different classes of substitutions at the different orders in the Møller–Plesset treatment to the asymptotic longitudinal second hyperpolarizability per H₂ unit in a.u. by using different atomic basis sets.

	$\Delta\gamma_2^D$	$\Delta\gamma_3^D$	$\Delta\gamma_4^S$	$\Delta\gamma_4^D$	$\Delta\gamma_4^T$	$\Delta\gamma_4^O$	$\Delta\gamma_4^{S+D+T+Q}$
STO-3G	-2244±3	-3706±7	-275±2	-1378±3	365±1	-246±1	-1533±3
(3)-21G	9976±22	-8398±2	-4±2	-4678±3	3291±4	-2209±5	-3603±1
(6)-31G	11 137±42	-7969±8	-176±14	-4534±7	3447±8	-2310±9	-3228±4
(6)-311G	13 616±106	-7512±44	534±28	-4327±30	3981±41	-2635±39	-2414±27
(6)-31G(*)*	15 723±57	-4784±91	1144±19	-2624±8	4416±10	-2892±9	52±1
(6)-311G(*)*	20 237±82	-3901±42	2102±69	-1910±15	5378±52	-3587±41	1982±33

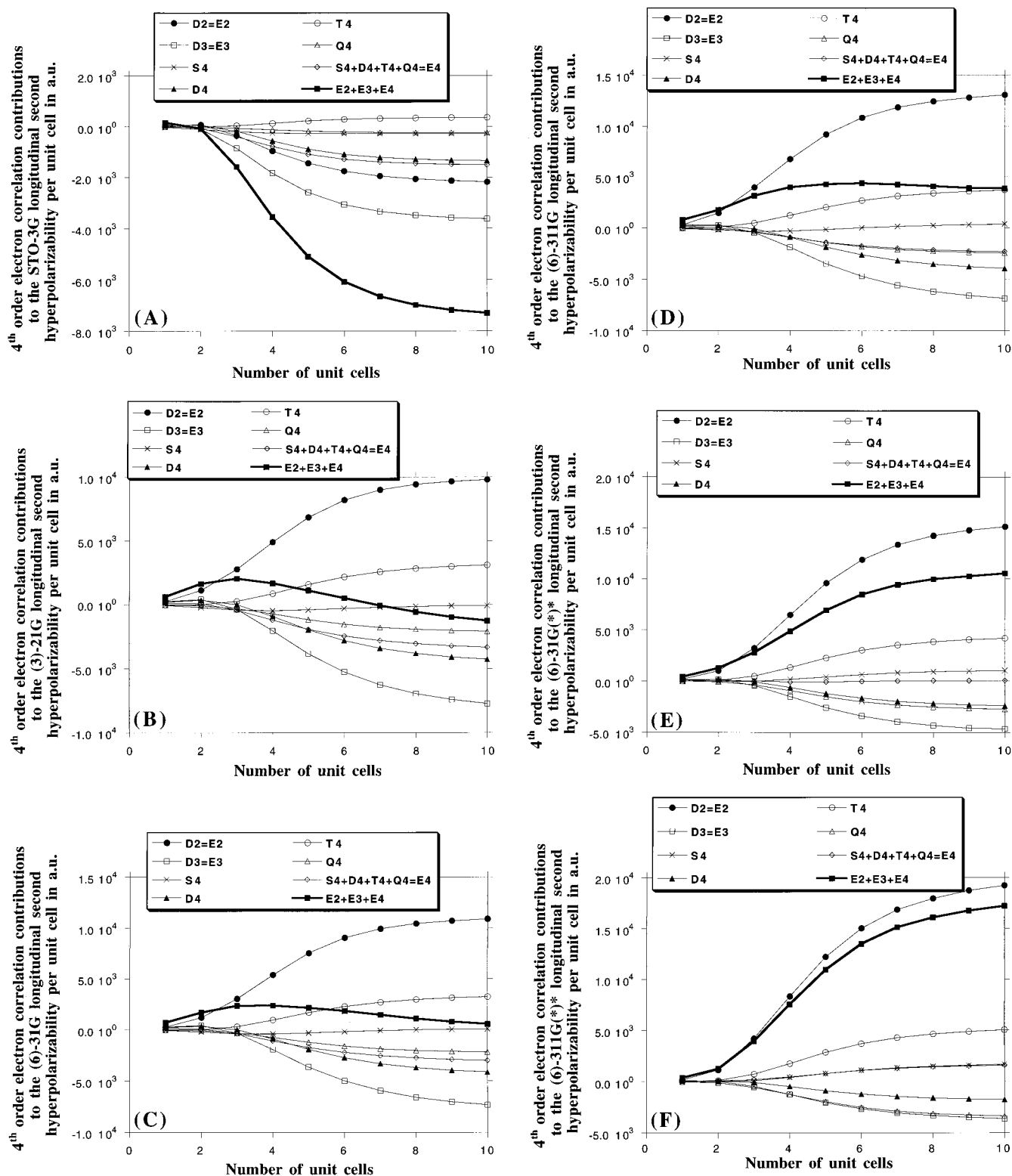


FIG. 3. Evolution with chain length of the different electron correlation corrections to the static longitudinal second hyperpolarizability per unit cell $\Delta\gamma_L(N) = \gamma_L(N) - \gamma_L(N-1)$ in a.u. of molecular hydrogen model chains by using different basis sets; (A) STO-3G, (B) (3)-21G, (C) (6)-31G, (D) (6)-311G, (E) (6)-31G(*), and (F) (6)-311G(*)

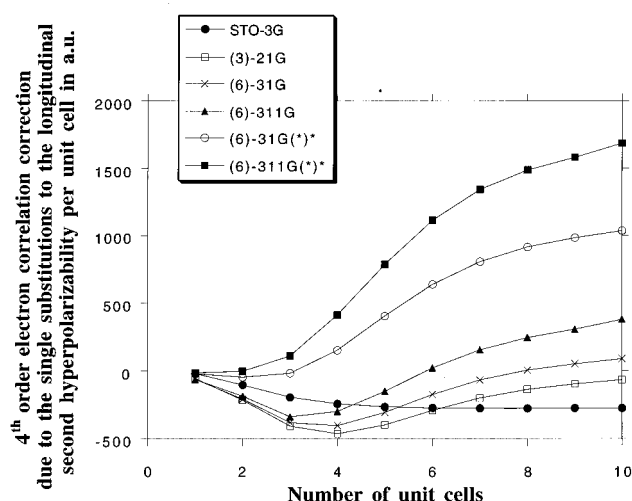


FIG. 4. Evolution with chain length of the fourth-order $\Delta\gamma_L(N)$ (given in a.u.) contribution due to the single substitutions according to the basis set.

contribution is positive and the largest for $\Delta\gamma_L$ whereas it is small and negative for $\Delta\alpha_L$. Whatever the basis set considered, the γ_4^T contribution is important and strongly modulates the total fourth-order contribution, determining even its sign for the (6)-31G(*)* and (6)-311G(*)* basis sets. Therefore, a SDQ-MP4 treatment of electron correlation is certainly not better than the MP3 treatment.

With the exception of $\Delta\gamma_4^S$ all the contributions per unit cell evolve with chain length like the total $\Delta\gamma_L$, i.e., they present an increase followed by a saturation regime and tend toward a plateau. For the global electron correlation corrections (Fig. 3) when considering the (3)-21G, (6)-31G, and (6)-311G basis sets as well as for the $\Delta\gamma_4^S$ contribution (Fig. 4) with all the basis sets apart from (6)-311G(*)* the $\Delta\gamma_L$ curves present a maximum/minimum for small chain length then decrease/increase before to reach a constant polymeric limit. No such behavior has been observed for $\Delta\alpha_L$. This difference of behavior can be understood by considering the SOS expressions of the polarizability and second hyperpolarizability [Eq. (4)]. For the polarizability, only one-photon excitations are involved and all these contribution are positive for the ground state wave function since the numerator is defined by squares of dipole transition strengths whereas the denominator corresponds to energy difference between singly excited states and the ground state. On the other hand, one-, two- and three-photon transitions describe the second hyperpolarizability [Eq. (4)] which can thus be composed of terms having different signs. Consequently, the inclusion of the electron correlation to different orders in electron-electron interactions and by different classes of substitutions do not play necessarily the same role on the different optical processes of γ and thus lead to maximum and/or minimum in their chain length dependence as it is here the case for some $\Delta\gamma_4^S$ and $\Delta\gamma_4$ curves.

IV. CONCLUSIONS AND OUTLOOK

Our initial investigation on hydrogen model chains of the effects of including electron correlation within the MP2,

MP3, and MP4 schemes on γ , by using different atomic basis sets ranging from the minimal STO-3G to the double- and triple-zeta basis sets augmented or not by one set of p -polarization functions has shown that γ is more difficult to evaluate than α and that electron correlation increases $\Delta\gamma_L$ by 30% mainly due to the second-order contribution. MP2 calculations carried out with a sufficiently extended basis set have been shown to provide most of the electron correlation correction. These effects have been compared with the MP2 electron correlation correction to the $\Delta\gamma_L$ of polyacetylene, polyene, and polypyrrole which are +90%, +420%, and +40%, respectively and which suggest that molecular hydrogen model chains with other bond length alternations deserve to be investigated to further assess the importance of electron correlation and the extent of the basis set required to include most of these corrections. Several *ab initio* studies on small molecules have shown that further electron correlation corrections are brought when considering infinite-order contributions due to the single, double,... substitutions in the framework of the coupled cluster approaches. This is particularly the case for molecules like ozone.⁵¹ As well as these conventional methods, the density functional approaches constitute a computationally cheaper way to include the electron correlation effects in the evaluation of the molecular response properties. An initial investigation of these density functional approaches for computing the linear polarizability of hydrogen model chains has shown the key role of the exchange potential.⁵⁵ In this way we could give an answer to the following two questions (i) at which level of theory is the prediction expected to provide meaningful values for the longitudinal second hyperpolarizability per unit cell of large oligomers?, and (ii) which atomic basis set is sufficiently extended for this considered electron correlation level?

Another direction of investigation of the electron correlation effects upon γ consists of comparing the relation between, on one hand, these Møller-Plesset and coupled cluster size-consistent techniques and, on the other hand, the numerous computational schemes based on truncated configuration interaction procedures which have been used many times within semi-empirical schemes to determine the non-linear responses of large oligomers and to analyze these SOS γ in terms of the most important optical processes.⁵⁶⁻⁶⁰ The slow saturation with chain length of $\Delta\gamma_L$ demonstrates the need to develop polymeric techniques which would make possible direct evaluation of the asymptotic $\Delta\gamma_L$ as is the case for the CHF and UCHF linear polarizability of stereoregular polymers.^{39-40,61} The persistent basis set effects between the (6)-31G(*)* and (6)-311G(*)* asymptotic $\Delta\gamma_L$ results show that saturation with respect to the basis set extent is not yet attained and that, to reach this purpose, more and more extended atomic basis sets such as the correlation consistent basis sets of Dunning and co-workers⁶² deserve to be utilized. Work along these lines is currently being undertaken in our laboratory.

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