Research Article

Electron Correlation Effects on the Longitudinal Polarizabilities and Second Hyperpolarizabilities of Polyenes: A Finite Field Study

Qingxu Li,[1] Xianju Zhou,[1] and Shiwei Yin[2]

[1] *College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, China*
[2] *School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China*

Correspondence should be addressed to Qingxu Li; liqx@cqupt.edu.cn

We carry out ab initio calculations, based on finite-field scheme, of the longitudinal polarizabilities (α_L) and second hyperpolarizabilities (γ_L) of conjugated polyenes, and study the effects of electron correlation, with second-order Moller-Plesset perturbation theory and coupled cluster with singles and doubles method. Calculations with density functional theory are also made to compare with wave-function based methods. Our study shows that electron correlation reduces linear longitudinal polarizability and enhances longitudinal second hyperpolarizability for short polyenes, but the effects decrease as the chain increases; choosing appropriate basis sets is important when quantitative results are required.

1. Introduction

The linear and nonlinear optical properties of conjugated polymers have been intensely investigated in recent decades due to their great potentials in industry. The polarizability and second hyperpolarizability of linear polyenes, the simplest conjugated polymer, have attracted research interests of many scientists. Ab initio calculations of linear α_L and γ_L are severely restricted to short polyenes due to the formidable computational costs. Hurst et al. reported ab initio coupled-perturbed HF (CPHF) calculations up to $C_{22}H_{24}$ more than 20 years ago [1]. Since then, researchers have showed that electron correlation effects play a key role in correctly describing the linear and nonlinear optical properties of conjugated systems [2–21]. And thus, proper treatment of electron correlation in electronic structure calculations is very important. However, accurate correlated electronic structure calculations for long polyenes require immense computational resources and thus are now impractical.

DFT method becomes more popular in recent years for its excellent balance between the accuracy and computational costs [22, 23]. Unfortunately, researches showed that DFT with commonly used xc-functionals always fails to offer a reasonable description of nonlinear optical properties for conjugated polymers, including polyenes [12–15]. In a recent work, Sekino et al. reported their efforts on developing new xc-functional to overcome this problem [15]. They also reported their calculations based on by MP2 (second-order Moller-Plesset perturbation theory) and CCSD (coupled cluster with singles and doubles method). Eventually, MP2 is the only practical choice for long polyenes till now. CCSD is more expensive and thus more restricted when used for evaluation of α_L and γ_L, even for the 6-31G basis set, the smallest basis set of practical use. Champagne et al. used MP2 method to invalidate DFT in evaluating α_L and γ_L of conjugated chains [12].

We found recently that, based on the semiempirical Pariser-Parr-Pople (PPP) model, CCSD predicts electron correlation results in a reduction on γ_L for long polyenes, while MP2 predicts electron correlation always enhances γ_L and thus gives wrong predictions for electron correlation contributions to the γ_L of long polyenes [9]. The primary ab initio CCSD calculations we made with 6-31G basis set lead to same conclusions to semiempirical PPP model.

Hurst et al. showed that basis sets of quasi-double zeta quality are good enough, particularly for the longitudinal component. Since their conclusion were based on CPHF calculations, we wonder if more reliable basis sets will still support this point. Calculations with various basis sets are thus performed and reported in this paper. Results obtained by three commonly-used DFT schemes are also presented for the sake of completeness.

2. Computational Details

The geometries of polyenes used in this study were taken from [12] (Figure 1(a) in [12]). Electronic energies for the system in different electric fields are calculated with Gaussian 03 package [24]. After that, the finite field method is used to evaluate the longitudinal polarizability (α_L) and second hyperpolarizability (γ_L) with the following numerical formulae:

$$\alpha_L = -\frac{E(\delta F) + E(-\delta F) - 2E(0)}{(\delta F)^2},$$

$$\gamma_L = -\frac{E(2\delta F) - 4E(\delta F) + 6E(0) - 4E(-\delta F) + E(-2\delta F)}{(\delta F)^4}.$$

(1)

The electric fields used are 0, 8, 16×10^{-4} a.u. (i.e., $\delta F = 8 \times 10^{-4}$ a.u). As is known, large electric field will result in troubles in convergence and small electric field will require more significant figures for numerical derivatives and consequently is more computationally expensive. We found $\delta F = 8 \times 10^{-4}$ a.u can work well for systems studied in this work. The electric field is applied along the direction of chain, as is chosen as x axis direction. Only longitudinal components $\alpha_{xx}(\alpha_L)$ and $\gamma_{xxxx}(\gamma_L)$ are calculated.

3. Results and Discussions

The results of longitudinal polarizabilities per unit cell α_L/N (N is number of unit cells or double bonds in the system) are gathered in Table 1. And the data obtained with 6-31G basis set are plotted in Figure 1. Champagne et al. reported their calculations in [12] for $C_{12}H_{14}$ and $C_{20}H_{22}$ with same geometries (double zeta basis set used for $C_{12}H_{14}$ and 6-31G used for the other, see details in [12]). DFT data reported here for $C_{20}H_{22}$ are exactly the same as those in [12] (all data mentioned here and after can be found in Tables 1–4 in [12]) as expected. Small differences (SVWN: 94.8, B3LYP: 87.0, reported in [12]) for $C_{12}H_{14}$ can attribute to different basis set used in calculations. This can also explain the difference between HF and MP2 results; besides, that coupled HF (CHF) was used in [12]. In Figure 1, all curves obtained by DFT schemes are above HF; however, MP2 and CCSD curves are below that of HF. One can easily see the failure of commonly used xc-fuctionals here, as was shown before by others [12–14]. SVWN and BLYP predict nearly identical results. Another point worth to mention is the difference between CCSD and MP2 increases as the chain grows. It becomes more important while quantitative or semiquantitative results
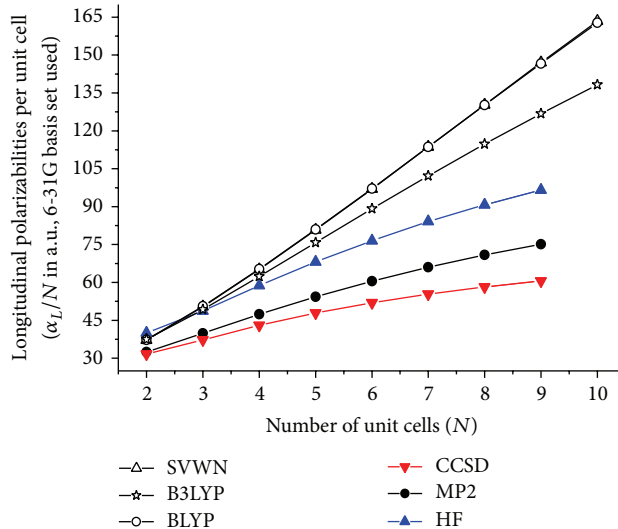

FIGURE 1: Longitudinal polarizabilities per unit cell (α_L/N) of polyenes (in a.u.) obtained by various quantum chemical methods with 6-31G basis set.
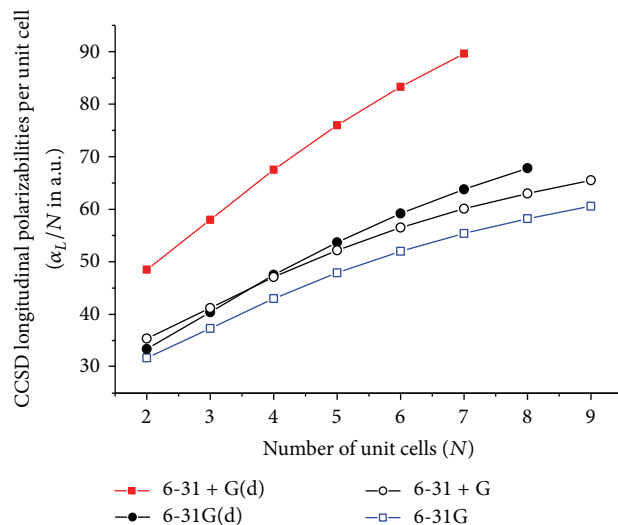

FIGURE 2: Longitudinal polarizabilities per unit cell (α_L/N) of polyenes (in a.u.) obtained by CCSD with various basis sets.

are required for long polyenes. Similar conclusions can be made for other basis sets from Table 1.

From Table 1, we conclude that basis set effects are unimportant for all DFT methods used here. Things are different for HF, MP2, and CCSD methods. We plot the CCSD results with various basis sets in Figure 2. The largest and also the most reliable basis set 6-31+G(d) is steeper than the other three ones. The differences between 6-31+G(d) basis set and other basis sets range from 27% to 38%. There are no essential difference between 6-31G, 6-31+G, and 6-31G(d) basis sets.

We now come to γ_L. The results are listed in Table 2, and the data obtained with 6-31G basis set are plotted in Figure 3. We first discuss results for 6-31G basis set. For DFT methods with 6-31G basis set, negligible differences

TABLE 1: Longitudinal polarizabilities per unit cell α_L/N of polyenes obtained by various chemical models (in a.u., N is the number of unit cells or double bonds in the system).

| N	2	3	4	5	6	7	8	9	10
6-31G									
HF	40.0	48.7	58.8	68.1	76.5	84.1	90.7	96.6	
MP2	32.5	39.9	47.4	54.3	60.5	66.0	70.9	75.1	
CCSD	31.7	37.3	43.0	47.9	52.0	55.4	58.2	60.6	
SVWN	37.2	50.4	65.1	80.8	97.0	114	130	147	163
BLYP	37.3	50.6	65.3	81.0	97.1	114	130	147	163
B3LYP	37.4	49.3	62.4	75.8	89.2	102	115	127	138
6-31G(d)									
HF	39.4	48.4	58.4	67.7	76.1	83.5	90.1		
MP2	33.5	42.0	50.6	58.7	66.1	72.8	78.7		
CCSD	33.4	40.4	47.5	53.7	59.2	63.8	67.8		
SVWN	37.4	51.1	66.0	82.0	98.6	116	133	150	167
BLYP	37.5	51.2	66.1	82.0	98.5	115	132	149	166
B3LYP	37.5	49.8	63.1	76.8	90.4	104	117	129	141
6-31+G									
HF	43.7	52.6	62.8	72.2	80.7	88.3	94.9	101	
MP2	36.8	44.5	52.3	59.5	65.9	71.7	76.7	81.1	
CCSD	35.4	41.2	47.1	52.2	56.5	60.1	63.0	65.5	
SVWN	41.6	55.3	70.4	86.5	103	120	137	154	171
BLYP	42.4	56.3	71.5	87.6	104	121	138	155	171
B3LYP	41.8	54.2	67.6	81.3	94.9	108	121	133	145
6-31+G(d)									
HF	56.4	68.4	81.8	94.1	105	115			
MP2	49.3	61.0	72.7	83.6	93.6	103			
CCSD	48.5	58.0	67.5	76.0	83.3	89.6			
SVWN	41.9	56.1	71.6	87.9	105	122	140	157	174
BLYP	42.7	57.1	72.6	89.0	106	123	140	157	174
B3LYP	42.1	54.9	68.6	82.6	96.5	110	123	135	147
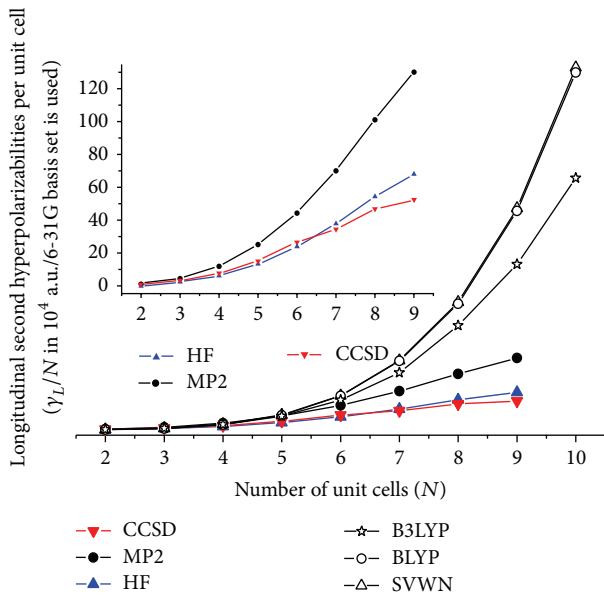
FIGURE 3: Longitudinal second hyperpolarizabilities per unit cell (γ_L/N) of polyenes (in 10^4 a.u.) obtained by various quantum chemical methods with 6-31G basis set.

appear when compared to those reported in [12]. One more thing to be mentioned here is that electric fields and numerical derivatives formulae will result in some differences on digitals. It is very interesting, seen from Figure 3, that CCSD calculations predict electron correlation will reduce γ_L while $N > 6$, fully contrary to those predicted by MP2, but the question is whether this point can be also confirmed by more reliable basis sets. Similar results can be found for calculations with 6-31+G basis set and now the sign inversion of correlation contribution occurs at $C_{18}H_{20}$, while, for 6-31G(d) and 6-31+G(d), this sign inversion has not been observed. One interesting problem then appears whether this sign inversion will occur or not for those two basis sets. If the answer is yes (we believe so), the commonly used MP2 (due to its moderate computational costs) makes qualitatively wrong predictions for correlation contribution on γ_L for long polyenes. Undoubtedly, further work is necessary to completely confirm this. The local CCSD method developed recently may be helpful to investigate the longer polyenes [10, 25–32].

In Figure 4, we plotted γ_L/N calculated by CCSD with various basis sets. Again, 6-31+G(d) basis set performs

TABLE 2: Longitudinal second hyperpolarizabilities per unit cell γ_L/N of polyenes obtained by various chemical models (in 10^4 a.u., N is the number of unit cells or double bonds in the system).

| N	2	3	4	5	6	7	8	9	10
6-31G									
HF	−0.12	1.93	5.85	12.9	23. 6	37.6	54.5	67.8	
MP2	0.84	4.33	11. 8	24. 9	44.4	70.2	101	131	
CCSD	0.80	3.11	7.44	15.3	26.5	34.5	46.7	52.3	
SVWN	0.15	2.80	9.91	26.9	61.8	126	232	403	659
BLYP	0.15	2.09	9.30	26.1	61.4	125	229	398	650
B3LYP	0.14	2.29	9.25	24.5	54.2	104	190	301	458
6-31G(d)									
HF	−0.11	1.79	5.38	11.9	21.4	33.9	49.3		
MP2	0.67	3.83	10.8	23.4	42.2	67.4	98.8		
CCSD	0.60	4.04	8.71	16.6	27.2	40.3	56.3		
SVWN	0.14	2.59	9.26	22.6	63.9	116	232	392	644
BLYP	0.13	2.57	9.25	23.1	60.0	121	231	384	637
B3LYP	0.12	2.63	9.07	23.5	51.6	99.2	173	278	422
6-31+G									
HF	0.42	3.56	8.78	17.4	30.0	45.5	62.3	85.2	
MP2	1.92	7.08	16.9	33.0	56.1	85.6	125	161	
CCSD	1.59	5.39	11.7	21.0	31.8	45.5	63.2	70.8	
SVWN	1.07	5.45	15.4	37.2	79.3	158	285	433	711
BLYP	1.18	5.71	16.9	40.0	83.2	159	357	468	728
B3LYP	0.98	5.30	15.2	35.1	69.0	148	216	335	497
6-31+G(d)									
HF	0.75	5.80	14.1	26.4	46.7	71.5			
MP2	2.88	11.1	26.8	51.5	91.5	141			
CCSD	2.70	9.01	19.5	35.3	59.3	89.0			
SVWN	1.08	5.26	14.76	35.5	76.0	148	269	450	709
BLYP	1.19	5.76	15.2	36.1	78.8	154	280	468	782
B3LYP	0.99	5.27	13.9	31.0	66.6	117	209	342	485
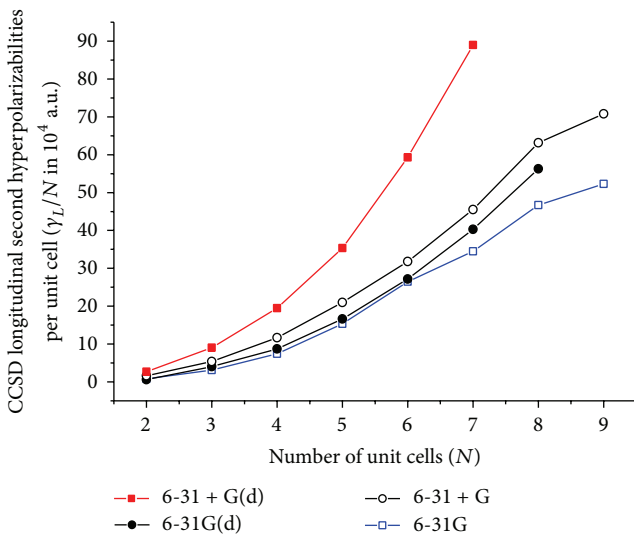
FIGURE 4: Longitudinal second hyperpolarizabilities per unit cell (γ_L/N, in 10^4 a.u.) obtained by CCSD with various basis sets.

obviously different from the other three. The difference for γ_L/N between 6-31+G(d) basis set and other basis sets ranges from 41% to 61%. And the 6-31G, 6-31+G, and 6-31G(d) basis sets perform similarly.

Sekino et al. reported their results based on CCSD calculations with cc-pVDZ basis set for polyenes up to $C_{12}H_{14}$ with a very different geometry (in the sense of bond length alternation) [15]. In their results, both CCSD and MP2 predict a positive correlation contribution for γ_L up to $N = 6$. Limacher et al. reported similar results based on calculations with response theory methods [33].

4. Conclusions

We have calculated the longitudinal polarizabilities and second hyperpolarizabilities of polyenes using HF, MP2, and CCSD methods and 6-31G, 6-31+G, 6-31G(d), and 6-31+G(d) basis sets. Both MP2 and CCSD predict a negative correlation contribution for longitudinal polarizability, while DFT calculations using SVWN, BLYP, and B3LYP schemes all

predicts positive correlation contributions. For second hyperpolarizability, a sign inversion of correlation contribution is observed for CCSD calculations with 6-31G and 6-31+G basis sets. This sign inversion is yet to be further confirmed by more reliable basis set in the future. Contrary to CCSD, MP2 predicts a positive correlation contribution and thus should be used with much caution for evaluation of second hyperpolarizabilities of long conjugated chains. Addition of diffuse and polarization functions will enhance γ_L obviously, but addition of polarization functions or addition of diffuse functions makes no essential difference.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
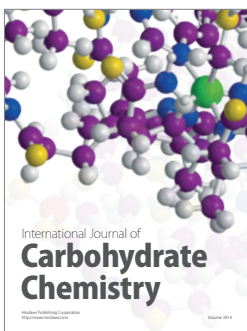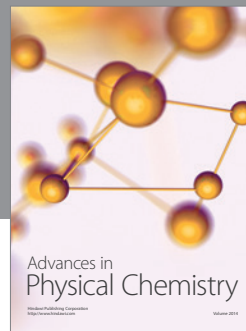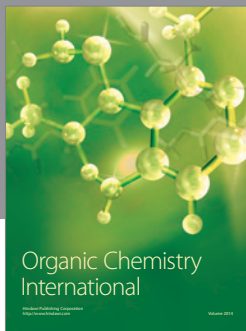
Acknowledgments

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