First hyperpolarizability of polymethineimine with long-range corrected functionals

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Using the long-range corrected (LC) density functional theory (DFT) scheme introduced by Iikura *et al.* [J. Chem. Phys. **115**, 3540 (2001)] and the Coulomb-attenuating model (CAM-B3LYP) of Yanai *et al.* [Chem. Phys. Lett. **393**, 51 (2004)], we have calculated the longitudinal dipole moments and static electronic first hyperpolarizabilities of increasingly long polymethineimine oligomers. For comparison purposes Hartree-Fock (HF), Møller-Plesset perturbation theory (MP2), and conventional pure and hybrid functionals have been considered as well. HF, generalized gradient approximation (GGA), and conventional hybrids provide too large dipole moments for long oligomers, while LC-DFT allows to reduce the discrepancy with respect to MP2 by a factor of 3. For the first hyperpolarizability, the incorrect evolution with the chain length predicted by HF is strongly worsened by BLYP, Perdew-Burke-Ernzerhof (PBE), and also by B3LYP and PBE0. On the reverse, LC-BLYP and LC-PBE hyperpolarizabilities are correctly predicted to be positive (but for the two smallest chains). Indeed, for medium and long oligomers LC hyperpolarizabilities are slightly smaller than MP2 hyperpolarizabilities, as it should be. CAM-B3LYP also strongly improves the B3LYP results, though a bit less impressively for small chain lengths. The present study demonstrates the efficiency of long-range DFT, even in very pathological cases. © 2007 American Institute of Physics. [DOI: [10.1063/1.2741246](https://doi.org/10.1063/1.2741246)]

Polymethineimine (PMI) $[-(\text{CH}=\text{N})_n-]$ is the simplest asymmetric isoelectronic polymeric parent of polyacetylene (PA). Long PMI chains are characterized by very large first hyperpolarizabilities (β),¹⁻³ and therefore they present a high potential for nonlinear optics (NLO) applications. However, an accurate evaluation of their NLO properties requires the inclusion of electron correlation (EC) effects that are extremely large, so large that they can even modify the sign of β .^{2,3} EC can be introduced through wave function based approaches [i.e., Møller-Plesset perturbation theory (MP), coupled-cluster (CC), etc.] but such strategies usually require very large computational resources for long oligomers as the use of extended basis sets (BSs) is often essential.⁴ A more appealing alternative is apparently offered by the density functional theory (DFT). However, since the works of Champagne *et al.*, it is well known that DFT calculations, using

conventional functionals, fail to correctly predict the amplitude of NLO properties of long organic materials.^{5,6} The problem is related to the exchange part of the functional that suffers from *short sightedness*: the DFT screening of the polarization charge induced by the external electric field at the chain ends is far from being adequate. To circumvent the problem, several approaches have been applied to the calculation of (N)LO properties: current-DFT formalism,⁷ optimized effective potential for exact exchange,^{8,9} and the computationally less demanding long-range (LR) functionals (LR-DFT).¹⁰⁻¹⁵ [In the following, we use LR-DFT as a generic name for both long-range correlated (LC) and Coulomb-attenuating model (CAM) approaches.] Recently, the Hirao group has demonstrated that their LC approach can be a powerful tool to evaluate the β of push-pull chains,¹³ as well as the second hyperpolarizability of PA.¹⁵ However, the evolution with the chain length of the β of PMI is even more challenging because both Hartree-Fock (HF) and conventional hybrids provide the incorrect sign for the medium chain length.³ Indeed, the correct values are not bracketed by

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TABLE I. Longitudinal dipole moments of all-*trans*-polymethineimine chains. All values are in au and have been computed with the 6-31G(*d*) basis set on the HF/6-31G(*d*) geometry (see Ref. 3). The HF, MP2, B3LYP, and PBE0 results come from Ref. 3. At the bottom of the table, the extrapolated values per unit cell of the polymer ($\infty \pm \Delta\infty$) are given.

<i>n</i>	HF	MP2	BLYP	PBE	B3LYP	PBE0	LC-BLYP	LC-PBE	CAM-B3LYP
2	0.525	0.360	0.333	0.331	0.372	0.382	0.367	0.371	0.389
4	1.478	0.999	0.990	0.989	1.095	1.121	1.086	1.095	1.137
6	2.713	1.820	1.866	1.867	2.058	2.105	2.035	2.049	2.130
8	4.133	2.768	2.921	2.922	3.207	3.276	3.143	3.163	3.297
10	5.673	3.806	4.123	4.123	4.496	4.586	4.358	4.386	4.584
12	7.296	4.909	5.445	5.455	5.891	5.998	5.649	5.683	5.958
14	8.975	6.059	6.862	6.876	7.364	7.485	6.994	7.035	7.394
16	10.695	7.244	8.355	8.372	8.895	9.028	8.378	8.426	8.874
18	12.445	8.455	9.905	9.926	10.470	10.611	9.790	9.844	10.387
20	14.216	9.686	11.500	11.525	12.076	12.226	11.223	11.284	11.924
22	16.003	10.930	13.128	13.158	13.707	13.863	12.672	12.740	13.479
24	17.802	12.186	14.782	14.817	15.356	15.517	14.133	14.207	15.048
26	19.611	13.449	16.457	16.496	17.020	17.185	15.602	15.683	16.628
28	21.426	14.720	18.147	18.190	18.694	18.863	17.079	17.166	18.215
30	23.247	15.996	19.849	19.897	20.377	20.549	18.561	18.655	19.808
∞	0.925	0.654	0.893	0.899	0.867	0.868	0.756	0.761	0.816
$\Delta\infty$	0.015	0.013	0.034	0.025	0.021	0.023	0.009	0.011	0.013

HF and B3LYP (or alike) results as it is the case for PA and push-pull systems: any simple HF/DFT combination seems to be doomed to failure. In this Communication, we test the efficiency of LC (Ref. 10) and CAM (Ref. 16) approaches for computing the electronic β of PMI oligomers.

The methodological tools used in this Communication have been described in detail previously,^{2,3,14} and we consequently provide a short summary only. We performed all LC (Ref. 10) and CAM (Ref. 16) calculations with the latest developmental version of the GAUSSIAN package,¹⁷ while the remaining computations have been performed with GAUSSIAN03.¹⁸ We restrict ourselves to the 6-31G(*d*) BS and the HF/6-31G(*d*) geometries for all-*trans*-conformers, to allow calculations on long oligomers as well as straightforward comparisons with previously published data.³ We refer the interested reader to Refs. 3 and 19 for the discussion about EC and BS effects on these geometries. We have only considered longitudinal properties in this work, as this component (denoted by the *L* subscript) clearly dominates the total response of PMI chains.²⁰ The vibrational contribution²¹ to β have been neglected at this stage; as a first description of the importance of this contribution in PMI is already available.²² The MP2 dipole moment (μ_L) and β_L have been determined through the numerical differentiation of the total energy computed under several external electric field strengths.² The DFT μ_L have been obtained from the standard expectation value formula whereas DFT β_L have been computed by using a finite-field procedure based on the numerical differentiation of the analytic polarizabilities evaluated with several electric field amplitudes.⁶ All DFT calculations have been performed with an *ultrafine* integration grid [pruned (99,590) grid]. The properties reduced per unit cell are defined as $\Delta X_L(n) = \frac{1}{2}[X_L(n) - X_L(n-2)]$ with $X = \mu$ or β . The polymeric properties (per unit cell) have been obtained by extrapolating the oligomeric values.²⁰

The dipole moments are listed in Table I and the evolu-

tion with the chain length of $\Delta\mu_L(n)$ is sketched in Fig. 1. For the dipole moments, CCSD(T) calculations using very large BS reveal that MP2 values are only too big by about 5%: The CCSD(T)/MP2 ratio are 0.96, 0.96, and 0.95 for $n=2, 4$, and 6, respectively.⁴ This conclusion is also supported by MP4 calculations using a smaller basis set.³ For chains longer than the tetramer, both HF and pure-GGA schemes overestimate μ_L by +49% (HF) and +8% (BLYP and PBE) for the decamer but by +41% (HF) and +37% (BLYP and PBE) for the polymer. Conventional hybrids

FIG. 1. Static longitudinal dipole moment per unit cell $\Delta\mu_L(n)$ for increasingly long polymethineimine chains.

TABLE II. Longitudinal first hyperpolarizabilities of all-*trans*-polymethineimine chains. All values are in au and have been computed with the 6-31G(*d*) basis set on the HF/6-31G(*d*) geometry (see Ref. 3). The HF, MP2, B3LYP, and PBE0 results come from Ref. 3. At the bottom of the table, the extrapolated values per unit cell of the polymer ($\infty \pm \Delta\infty$) are given.

<i>n</i>	HF	MP2	BLYP	PBE	B3LYP	PBE0	LC-BLYP	LC-PBE	CAM-B3LYP
2	-56	64	-33	-36	-33	-36	-16	-20	-25
4	-378	653	-910	-910	-608	-554	-63	-67	-255
6	-912	2 390	-5 930	-5 910	-3 109	-2 638	106	112	-780
8	-1297	5 890	-21 076	-21 023	-8 595	-6 829	1 103	1 138	-1 068
10	-1281	11 494	-52 919	-52 866	-16 582	-12 824	3 429	3 513	-343
12	-797	19 192	-104 948	-105 011	-25 201	-17 458	7 269	7 422	1 916
14	122	28 764	-174 642	-175 020	-32 306	-20 678	12 575	12 813	5 875
16	1 408	39 917	-253 619	-254 515	-36 397	-21 091	19 185	19 522	11 459
18	2 991	52 355	-330 870	-332 328	-36 820	-18 444	26 903	27 349	18 486
20	4 810	65 829	-397 059	-399 167	-33 611	-12 900	35 539	36 102	26 739
22	6 813	80 119	-446 940	-449 430	-27 088	-4 804	44 920	45 606	36 010
24	8 960	95 049			-17 710	5 496	54 899	55 713	46 111
26	11 218	110 487			-5 941	17 587	65 359	66 306	56 887
28	13 562	126 318					76 199	77 281	68 203
30	15 975	142 468					87 349	88 570	79 960
∞	1 426	9 171					7 071	7 148	7 792
$\Delta\infty$	159	796					896	904	1 004

B3LYP and PBE0 do not improve the pure-GGA estimates (+33% in the polymer). On the contrary, LC and CAM approaches are much more satisfying, although they still overshoot the longitudinal dipole by +16% and +25%, respectively, when n reaches ∞ . For extended molecules the LC approach basically reduces the GGA error on μ_L by a factor of 2.3. In addition, the LC μ_L are much more consistent with the MP2 results. Indeed, the LC-PBE curve almost parallels the MP2 line in Fig. 1: Between $n=6$ and $n=30$ the overestimation is always bracketed by the +16% and +18% limits [for $\Delta\mu_L(n)$] whereas in the same time the PBE error goes from +7% to +33%.

PMI polarizabilities computed with LR-DFT have recently been published,¹⁴ and it has been found that both LC and CAM methodologies were very satisfying.

The β_L computed within several computational schemes are compared in Table II and the corresponding evolution with the chain length of $\Delta\beta_L(n)$ is plotted in Fig. 2. The β_L of the dimer, tetramer, and hexamer are positive at the MP and CC levels.⁴ In addition, CCSD(T) calculations demonstrate that the MP2 β_L is too large by about 35% for the hexamer (this percentage apparently decreases with chain length).⁴ This is consistent with other MP4 estimates.^{2,3} All the MP2 β_L systematically have the correct sign though their amplitude is too large by about 30% for medium chain lengths. The set of β_L listed in Table II illustrates the doom of conventional DFT: For $n=12$, MP2 predicts a $+19 \times 10^3$ au β_L whereas both GGA yield -105×10^3 au, that is an error of 653%. Full-range hybrids correct this behavior but to a much too small extent: -25×10^3 au (232%) with B3LYP and -17×10^3 au (189%) with PBE0. This glaringly appears on Fig. 2: BLYP and B3LYP actually accentuate the incorrect HF evolution instead of correcting it. Indeed, both functionals provide the wrong direction for the EC corrections to β_L . As up to $n=12$, both GGA and HF predict the incorrect sign for β_L ; any straightforward combination is

likely to be useless. On the contrary, LC and CAM accurately foresee the direction of the EC effects for all chain lengths. In addition, the LC-BLYP and LC-PBE β_L and $\Delta\beta_L$ are only negative for the dimer and tetramer but positive for longer chains. These negative values for $n=2$ and $n=4$ are probably related to a (slightly) overestimated chain-end contribution, as in the HF model.² The LC-BLYP and LC-PBE evolutions with chain length are also much more reasonable than that of B3LYP and PBE0: they parallel the MP2 curves but with smaller absolute values (Fig. 2). For the polymer the LC-BLYP $\Delta\beta_L$ is 23% smaller than the MP2 response, i.e., it

FIG. 2. Static longitudinal first hyperpolarizability per unit cell $\Delta\beta_L(n)$ for increasingly long polymethineimine chains.

lies in the correct region, close to the values obtained by sophisticated post-HF (MP4 and CC) approaches. CAM-B3LYP $\Delta\beta_L(n)$ are similar to HF for short chains, but qualitatively follows the MP2 curve when $n \geq 10$. Therefore, LR-DFT schemes are much more efficient than GGA or conventional hybrids for evaluating the NLO properties of medium and large PMI chains. In addition, the convergence of the finite-field calculations is much easier with LR-DFT, allowing computations on more extended systems.

The longitudinal dipole moments and static electronic first hyperpolarizabilities of short, medium, and long polymethineimine chains computed with various DFT functionals have been compared to HF and MP2 results. It turns out that LC-DFT approximations significantly reduce the GGA error for the dipole moments whereas full-range hybrids only allow a small correction. Except for the dimer and tetramer, LC first hyperpolarizabilities are positive and slightly smaller than the MP2 values, indicating an accurate evolution with the chain length. This is a remarkable result; as up to $n=12$, HF, GGA, and conventional hybrids all provide the incorrect sign for β_L : LC-DFT restores the correct balance between chain ends and unit cells contributions,³ although the correct values are not bracketed by the HF and GGA results. CAM-B3LYP also significantly improves the B3LYP estimates, especially for β_L , though not as striking than LC for short chain lengths. Together with our previous investigation,¹⁴ this Letter shows that, for the few pathological cases in which traditional hybrid functionals become unsatisfying, LC and CAM functionals could probably allow a significant accuracy improvement.

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