

## Electric Field Dependence of the Exchange-Correlation Potential in Molecular Chains

S. J. A. van Gisbergen,<sup>1</sup> P. R. T. Schipper,<sup>1</sup> O. V. Gritsenko,<sup>1</sup> E. J. Baerends,<sup>1</sup> J. G. Snijders,<sup>2</sup>  
B. Champagne,<sup>3</sup> and B. Kirtman<sup>4</sup>

<sup>1</sup>*Section Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*

<sup>2</sup>*Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

<sup>3</sup>*Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61,  
B-5000 Namur, Belgium*

<sup>4</sup>*Department of Chemistry, University of California, Santa Barbara, California 93106*

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Density functional calculations on the (non)linear optical properties of conjugated molecular chains using currently popular exchange-correlation (xc) potentials give overestimations of several orders of magnitude. By analyzing “exact” and Krieger-Li-Iafrate xc potentials, the error is traced back to an incorrect electric field dependence of the “response part” of the xc potential in local and gradient-corrected density approximation, which lack a linear term counteracting the applied electric field.

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The nonlinear optical (NLO) properties of molecules are of considerable current interest, both from the fundamental and technological points of view [1–3]. Prototype systems exhibiting large NLO responses like the polyacetylene (PA) chains have been studied intensively with conventional, *ab initio* Hartree-Fock (HF) based theoretical techniques [2]. Because density functional theory (DFT) [4,5] usually provides clearly improved accuracy with respect to HF at similar or lower computational cost, it seems tempting to apply DFT to the prediction of the NLO properties of large, conjugated molecular chains.

Our calculations on static hyperpolarizabilities (determining the NLO response in the static limit) of such chains show, both here and in Ref. [6], that the local density approximation (LDA) and generalized gradient approximations (GGAs) in DFT provide very poor results. Whereas previously reported LDA errors are typically 10% for dielectric constants, we find overestimations of several orders of magnitude for the second hyperpolarizability  $\gamma$ . In view of the respectable accuracy which is usually obtained in DFT calculations, this is highly surprising and deserves a detailed analysis, as this error may be among the largest in the history of DFT calculations. Our analysis allows us to pinpoint the weakness of the LDA. It will be shown below that, if an electric field,  $E$ , is applied, the so-called response part of the exact exchange-correlation (xc) potential develops a global behavior counteracting the applied field. Such behavior is not present in the LDA or GGA potentials. Our results substantiate and further elucidate the findings of Gonze, Ghosez, and Godby [7] and others [8–13], who pointed out the existence of such a counteracting linear potential in the exact  $v_{xc}$  and provided the first physical interpretation for it [10,13].

*Description of the problem.*—For this work, extensive calculations have been performed on PA and hydrogen chains. The LDA results described below have been

obtained in the same manner as earlier calculations on the polarizability ( $\alpha$ ) and second hyperpolarizability ( $\gamma$ ) of  $C_{60}$  [14]. Details of the computational procedure, the geometries, etc., have been given in another paper [6], where several aspects of the LDA problem (size of electron correlation correction, effect of bond length alternation) are described more fully.

From the HF-based *ab initio* studies [15] on the NLO properties of PA chains, it is known that even simple HF theory provides results which are in qualitative agreement with the more advanced [16] Møller-Plesset (MP) and coupled cluster calculations. The problem with the LDA and GGA xc potentials can be clarified by comparing the LDA and HF results for  $\alpha$  and  $\gamma$  of PA chains ( $C_{2n}H_{2n+2}$ ), with a varying number of unit cells  $n$ . This is done in Fig. 1, where the HF values for  $\alpha$  and  $\gamma$  [15] at a chain length of 20 C atoms have been normalized to 1. The LDA polarizability  $\alpha$  (in a double zeta basis) is overestimated for each chain length  $n$ , and this overestimation increases with  $n$ . The same trends are magnified for the second hyperpolarizability tensor  $\gamma$ , which is larger by a factor of 60 for the  $C_{44}H_{46}$  molecule, and continues to increase significantly for larger chains (we have gone up to  $C_{58}H_{60}$ ).

Previous error estimates for the LDA values ranged over roughly a factor of 2 for (first) hyperpolarizabilities [17], implying that qualitatively correct predictions can be obtained. Our results, giving overestimations of several orders of magnitude, show that this is not always the case. It is especially disconcerting that the LDA errors are so large for systems which are of most interest, i.e., those exhibiting large nonlinear polarization. If DFT is to play a useful role in understanding the NLO properties of these important systems, a detailed investigation is needed in which the deficiencies of the LDA and related potentials are pinpointed.

*Analysis of “exact” xc potentials.*—In this section, we analyze exact (very accurate) xc potentials, constructed

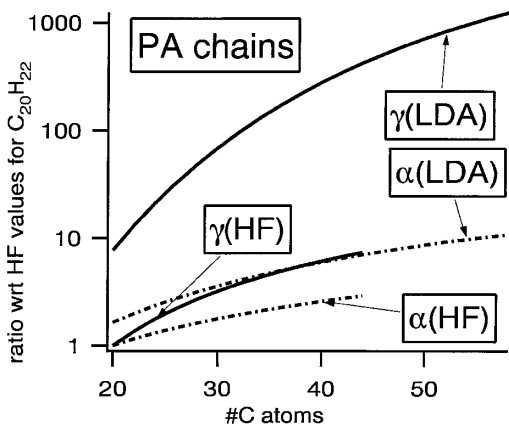


FIG. 1. (Hyper)polarizabilities of  $C_{2n}H_{2n+2}$  in HF geometry [16] given as a ratio to HF values (with 6-31G-SV basis) for  $C_{20}H_{22}$  of  $\alpha^{\text{HF}} = 1000$  a.u. and  $\gamma^{\text{HF}} = 894 \times 10^3$  a.u.

from *ab initio* configuration interaction (CI) densities according to the scheme of Ref. [18].

Our analysis started with the observation [6] that GGA potentials, or the asymptotically correct (behaving as  $-1/r$  for large  $r$ ) LB94 xc potential [19], do not improve upon LDA (thus showing that the problem is unrelated to the slight LDA overestimation for small molecules [20]). We then constructed, for linear polyene and hydrogen chains, xc potentials reproducing HF and CI densities in the presence or absence of an external field. A term linear in the field was found to occur in these potentials, suggesting that the problem is related to the one first discussed by Gonze, Ghosez, and Godby [7], which evoked a lot of discussion in the recent literature [9–13]. They state that for an infinite system in an electric field, in a correct treatment, a linear term will arise in the exact xc potential [see also Eq. (5) of Ref. [13]], which cannot be captured by a functional dependence on the periodic bulk density alone. This has led to the development of polarization-dependent density functional theory, which is a generalization of DFT taking the polarization of the system into account.

Our approach evades the concept of a metastable state and the ensuing problems with respect to the Hohenberg-Kohn theorem introduced in previous papers [7], as we consider molecules in the ground state in electric fields which may, because of the exponential decay of the basis functions, be considered to rapidly decay outside the molecule. Furthermore, we construct our potentials from accurate CI densities of real molecules, instead of using model Hamiltonians and densities [7]. In our analysis, we realize the thought experiment of Ref. [11] by considering finite systems (approaching the infinite system in the limit), in which case no extensions of ordinary DFT are needed.

Our analysis starts from the xc energy  $E_{\text{xc}}$  expressed in terms of the coupling constant integrated pair correlation function  $\bar{g}$ ,

$$E_{\text{xc}} = \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)[\bar{g}(\mathbf{r}_1, \mathbf{r}_2) - 1]\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (1)$$

A detailed explanation for the origin of the linear term will be obtained by using the decomposition of  $v_{\text{xc}}$  [where  $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}/\delta\rho(\mathbf{r})$ ] as in [21],

$$\begin{aligned} v_{\text{xc}}(\mathbf{r}) &= \bar{v}_{\text{xc}}^{\text{hole}}(\mathbf{r}) + v^{\text{resp}}(\mathbf{r}) \\ &= \int \frac{\rho(\mathbf{r}_1)[\bar{g}(\mathbf{r}, \mathbf{r}_1) - 1]}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 \\ &\quad + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{\delta\bar{g}(\mathbf{r}_1, \mathbf{r}_2)}{\delta\rho(\mathbf{r})} d\mathbf{r}_1 d\mathbf{r}_2, \quad (2) \end{aligned}$$

where  $\bar{v}_{\text{xc}}^{\text{hole}}$  is the potential of the coupling constant integrated xc hole. The second term on the right-hand side is called the “response potential.”

In order to establish the existence of a linear term in a finite system and trace its origin, it is necessary to consider small systems, for which truly high-level CI densities can be constructed. To this purpose, we considered the simple H-H and H<sub>2</sub>-H<sub>2</sub> cases, allowing us to make statements about the  $x$  vs  $c$ , and hole vs response nature of the linear term. First, a system of two distant H atoms in a field was considered. This system has the one-electron level of one H atom shifted down by the field with respect to the other one. It is therefore analogous to a dissociating heteronuclear diatomic molecule. A reasoning similar to the one given in Ref. [22] for a heteronuclear diatomic molecule (cf. Ref. [23]) shows that a step will arise in the xc potential, which counteracts the down-shift and is related to the *correlation part of the response potential*. This step (confirmed numerically in our full CI test calculations) represents the effect of long-range left-right electron correlation, which prevents localization of both electrons on the down-field H atom.

A similar reasoning for two widely spaced closed shell atoms or molecules leads to a zero step, in accordance with the absence of a long-range left-right correlation in that case. However, at shorter distances, where the *exchange* interaction between the closed shell molecules becomes important, a step again appears in  $v_{\text{xc}}$ . This counteracting term, which emerges in the response part of the exact xc potential if a field is switched on, is displayed in Fig. 2 for an H<sub>2</sub>-H<sub>2</sub> system at a separation of 3.0 bohrs (H-H distance is 1.4 bohrs). In plots similar to Fig. 2, but with larger H<sub>2</sub>-H<sub>2</sub> distances, the magnitude of the step decreases. This is in agreement with the analysis above that a step in the response potential should disappear in the limit of infinite separation for closed shell systems. This behavior for varying H<sub>2</sub>-H<sub>2</sub> separation explains the previously poorly understood fact that the GGA results for  $\alpha/n$  of hydrogen chains in Ref. [24] differ with respect to the HF values by a factor of 2.53 at an H<sub>2</sub>-H<sub>2</sub> separation of 2.5 bohrs, while the factor is only 1.23 at an H<sub>2</sub>-H<sub>2</sub> separation of 4.0 bohrs. In short, a term counteracting an external field as found in longer chains appears already in the response potential of the simple H-H and H<sub>2</sub>-H<sub>2</sub> systems. In the former it is a pure correlation effect, while for the latter, the effect of exchange will be dominant

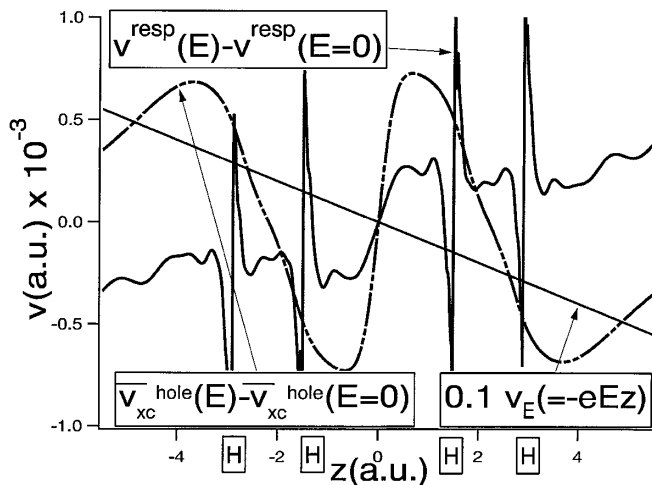


FIG. 2. Changes, due to an electric field of 0.001 a.u. in response and hole potentials for  $H_2-H_2$ , constructed from multireference CI singles doubles density with a large (cc-pV6Z without  $d$  and  $f$  functions) basis set, compared to the applied field (potential  $v_E$ ).

[Krieger-Li-Iafrate (KLI)  $x$  potential [25] (see below) plots for  $H_2-H_2$  display the same features as Fig. 2].

On the other hand,  $\bar{v}_{xc}^{\text{hole}}$  is dominated by the cancellation of the self-interaction (SI) embodied in the Hartree potential. This cancellation is already contained in the exchange part. In a two-electron case like  $H_2$ , the exchange hole contains only an SI part (the  $x$  potential is minus half the Hartree potential). Polarization of the charge density in an electric field generates a Hartree potential for  $H_2$  that counteracts the field, but an  $x$  hole potential has the same direction as the field. This is clearly visible within each  $H_2$  molecule in Fig. 2 (compare  $v_{xc}^{\text{hole}}$  to the applied potential  $v_E$ ). Therefore, the induced changes in  $\bar{v}_{xc}^{\text{hole}}$  cannot give an explanation for the counteracting nature of the linear term. Earlier interpretations of the emerging linear term in terms of a “polarization of the xc hole” [10,13] therefore cannot refer to the change induced in  $\bar{v}_{xc}^{\text{hole}}$ , i.e.,  $\bar{g}$ , but should be interpreted as referring to the response potential of Eq. (2), i.e., the derivative of  $\bar{g}$ .

*KLI potential as first solution.*—The key role of the response potential thus being established on the basis of rigorous properties of the xc potential and exact xc calculations, we turn for further analysis to approximate functionals which can be expected to give a good representation of the true response potential. One may both hope that such functionals will improve considerably upon the LDA results and expect to learn more about the origin of the counteracting term. The important KLI [25] potential, which is considered to be a very good approximation to the exact  $x$ -only potential, is one of the few functionals which can be expected to give a reasonable approximation also to the response part of the potential, as it exhibits many features also shown by the full exact  $x$ -only potential, or optimized effective potential [26]. Furthermore, the fact that xc potentials constructed from HF densities already yield a

counteracting term indicates that an important part of the desired effect should already be observed at the  $x$ -only level. The KLI potential has the following functional form (see Ref. [25] for details):

$$v_x^{\text{KLI}}(\mathbf{r}) = v_x^{\text{hole}}(\mathbf{r}) + \sum_{i=1}^{N_{\text{occ}}-1} w_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})}, \quad (3)$$

where the potential of the Fermi hole  $v_x^{\text{hole}}(\mathbf{r})$  assures the correct asymptotic  $-1/r$  behavior, typical for self-interaction-free xc potentials such as KLI, while the second part is the exchange contribution to the response potential, which tends exponentially to zero for large  $r$ .

In Fig. 3, the KLI potential for  $H_{18}$  in a field is presented. As in the accurate xc potentials, it clearly exhibits a counteracting term analogous to the step function we have found in  $H_4$ . This term arises from the response part of this potential. Figure 3, as well as similar plots for shorter hydrogen and polyene chains, shows no global linear field term in  $v_x^{\text{hole}}$  at the field strength used here. Consequently, the linear term is unrelated to the SI cancellation.

In fact, the linear term arises from the polarization of the Kohn-Sham (KS) orbitals in the field which does not significantly change the density in the center of the chain. This can be understood as follows: If, in the occupied orbital space, one has both a bonding “ $a + b$ ” atomic orbital combination and an antibonding “ $a - b$ ” combination, an electric field will mix them. One obtains an orbital of largely “ $a$ ” character at lower energy than the original “ $a + b$ ” orbital and a largely “ $b$ ” orbital at higher energy than the original “ $a - b$ ” orbital. The sum density of these orbitals remains unchanged, but in the KLI approximation to the response potential, this occupied-occupied mixing leads to a counteracting potential, due to the fact that the KLI weights  $w_i$  are larger for

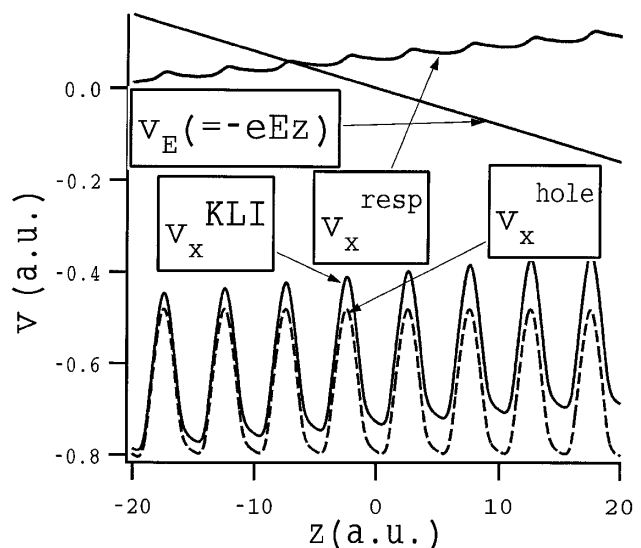


FIG. 3. Constituent parts of the KLI potential of  $H_{18}$  in an electric field, with a 6-311++G\*\* basis. The H atoms are at alternating distances of 2 and 3 bohrs (central pair at  $\pm 1.0$  bohrs).

TABLE I. Comparison of various results for  $\alpha$  and  $\gamma$  of  $H_{18}$ .

Method	Basis set	$10^{-3}\gamma$ (a.u.)	$\alpha$ (a.u.)
LDA	Basis set limit estimate	4300	367
KLI	6-311++G**	$700 \pm 100^a$	$261 \pm 1^a$
HF	6-311++G**	302	222
MP4 [27]	6-311G(*)	382	205

<sup>a</sup>Determined from finite field expansion of dipole moment.

the deeper-lying orbitals, which are more localized in the down-field region. This picture is consistent with our calculations which show that the applied field causes large mixing between the occupied orbitals and strong localization of the lowest energy orbitals, which have larger KLI weights  $w_i$ , to the down-field side of the chain. Although the KLI potential is local (multiplicative), it can provide the required ultra-non-local density dependence through its weights  $w_i$  and its orbital density dependence.

Having established the qualitatively correct behavior of the KLI potential, we turn to its performance in actual calculations. The KLI, LDA, HF, and MP4 results for  $\alpha$  and  $\gamma$  of  $H_{18}$  are given in Table I. The KLI results for both  $\alpha$  and  $\gamma$  considerably improve upon LDA (for  $\gamma$  the improvement is a factor of 6). However, the results are still not close to the HF and higher-level *ab initio* results [27]. In smaller chains, such as  $H_6$ , we find  $\gamma = 31.3, 29.7 \pm 0.2, 36.7 \pm 0.2$ , and  $99.7 \pm 0.2 \times 10^3$  a.u., for, respectively, MP4 [27], HF, KLI, and LDA, while for  $H_{12}$  these numbers are 179,  $147 \pm 2$ ,  $300 \pm 50$ , and  $1250 \pm 50 \times 10^3$  a.u., showing that the LDA failure increases with chain length and that the problem is not restricted to conjugated molecules such as PA. In all cases, the KLI results partially correct the LDA/GGA overpolarization (which we largely attribute to the linear term in this potential), but are still larger than the benchmark values. These results imply that either the KLI potential is not yet a sufficiently good approximation to the exact KS  $x$  potential, or that the correlation effects which were shown to be important for weak bonds ( $H \cdots H$ ) cannot be neglected here.

Finally, we note that the observed problem also affects low-lying excitation energies. In LDA test calculations on PA chains, we found these to be increasingly underestimated for larger chains, in accordance with our (hyper)polarizability results. Through the excitation energies, the problem also has serious consequences for many other response properties.

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