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# Simple charge-transfer model to explain the electrical response of hydrogen chains

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Linear $H_{2n}$ chains of $H_2$ units are experimentally unrealizable but simple and widely studied exemplars of the response coefficients (polarizabilities and hyperpolarizabilities) of polymer chains in uniform longitudinal electric fields. They show two surprising features: (1) Their response coefficients, unlike those of bulk solids, show a strong nonlinear dependence upon length or $n$. (2) Their response coefficients are seriously too large when computed with standard local or semilocal density functionals, but are much more correct when computed with self-interaction-free approaches (including Hartree-Fock). We propose a simple charge-transfer model which explains both of these effects in analytic terms. In this model, charge is transferred between $H_2$ units paired up at equal distances from but on opposite sides of the chain center. All symmetric pairs of $H_2$ units, not just the one for the chain ends, are included. This transfer is driven by the external electric field, and opposed by the chemical hardness of each $H_2$ unit. Unlike the situation in a bulk solid, this charge transfer is not suppressed (or even much affected) by electrostatic interactions among the transferred charges for $n \leq 7$. Self-interaction-free approaches increase the chemical hardness of an $H_2$ unit in comparison with semilocal density functionals, and so reduce the charge transfer. The physical picture behind the model is validated and its limitations are revealed by an analysis of the charge density from self-consistent electronic structure calculations. An appendix presents an accurate method to extract the hyperpolarizability from self-consistent calculations, and its results.

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## I. INTRODUCTION

When a centrosymmetric linear molecular chain is placed in a longitudinal weak electric field $F$, its energy is lowered by

$$\Delta E = -\tfrac{1}{2}\alpha F^2 - \tfrac{1}{24}\chi F^4, \tag{1}$$

where $\alpha$ is the polarizability and $\chi$ is the second hyperpolarizability (important for nonlinear optics). Typically $\alpha$ and $\chi$ show a strongly nonlinear dependence upon chain length [1–7], although a parallel stacking of long chains to make a three-dimensional solid would show a linear dependence.

Standard semilocal density functionals like the local spin-density approximation (LSD) [8] and the generalized gradient approximation (GGA) [9] work well for many problems, but seriously overestimate $\alpha$ and especially $\chi$ for molecular chains, while Hartree-Fock (HF) or exact-exchange approximations and the Perdew-Zunger self-interaction correction (SIC) [10–15] to the semilocal approximations perform much better [1–7,16]; see also Appendix A. (SIC is also important for molecular electronics [17].)

These facts are well known, but perhaps not so well understood. Here we will present a simple charge-transfer model which explains them qualitatively, confirming the arguments of Refs. [3,7,16]. Thus we emulate an older and currently less-followed tradition of theoretical physics, in which semiquantitative analytic models are used to test and confirm physical insights into the results of real or numerical experiments. The model is based on and tested for the linear $H_{2n}$ chains that were proposed in Ref. [1] as exemplars of real polymer chains. In $H_{14}$, for example, LSD overestimates the hyperpolarizability by more than a factor of 10. Our model is too simple for many quantitative or predictive purposes, but not for explanatory ones. The failure of semilocal functionals for charge-transfer problems is a well understood [18] consequence of self-interaction errors.

Atomic units are used throughout this paper. The conversion factors for SI units are the following: energy, 1 hartree $=4.359\,748\times10^{-18}$ J; length, 1 bohr$=0.529\,177\times10^{-10}$ m; dipole moment, $1ea_0=8.4784\times10^{-30}$ C m; octapole moment, 1 a.u.$=2.3742\times10^{-50}$ C m$^3$; polarizability $\alpha$, 1 a.u. $=1.6488\times10^{-41}$ C$^2$ m$^2$ J$^{-1}$$=0.148\,18$ Å$^3$; second hyperpolarizability $\chi$, 1 a.u.$=6.2354\times10^{-65}$ C$^4$ m$^4$ J$^{-3}$.

## II. CHARGE-TRANSFER MODEL FOR $H_{2n}$ CHAINS

Consider a linear chain of $H_2$ units. Each $H_2$ unit is a “molecule” of bond length 2 bohr, and is separated from the next $H_2$ unit by 3 bohr, where both lengths are measured between nuclei. An $H_{2n}$ chain has an integer number $n$ of such units, each of length $l_0=5$ bohr.

Each $H_2$ unit is assumed identical to every other $H_2$ unit within a chain of given size $n$. There are two kinds of charge transfer, *within* an $H_2$ unit and *between* two $H_2$ units, which will be modeled separately. In the absence of charge transfer between $H_2$ units, and neglecting interaction among the $H_2$ units, the total energy change due to a uniform longitudinal electric field $F$ is $n$ times the change per unit. Thus the total polarizability and hyperpolarizability in the absence of charge transfer are interpolated linearly as $\alpha=\alpha_1+\bar{\alpha}(n-1)$ and $\chi=\chi_1+\bar{\chi}(n-1)$. Here $\alpha_1$ and $\chi_1$ are the values for $n=1$, while $\bar{\alpha}$ and $\bar{\chi}$ are the values per $H_2$ unit for $n=\infty$.

Now allow charge transfer between two $H_2$ units located symmetrically on opposite sides of the chain center. Let $l$ be the distance between the centers of these two units, and let $\delta$

electrons be transferred in the direction opposite to $F$, from the center of one $H_2$ unit to the center of the other. Neglecting for a moment the electrostatic interaction between the transferred charges, the electrostatic energy is lowered by the change $-Fl\delta$. The energy of each unit in the absence of field is assumed to have an expansion in powers of $\delta$ through order $\delta^4$. The energy of the unit that acquires $\delta$ electrons is changed by $\mu_1\delta+\mu_2\delta^2+\mu_3\delta^3+\mu_4\delta^4$, while that of the unit that loses $\delta$ electrons is similarly changed by $\mu_1(-\delta)+\mu_2(-\delta)^2+\mu_3(-\delta)^3+\mu_4(-\delta)^4$.

To find $\delta$, we must minimize the total energy change

$$\Delta = 2\mu_2\delta^2 + 2\mu_4\delta^4 - Fl\delta. \tag{2}$$

Here $\mu_2 > 0$ is proportional to the "chemical hardness" [19–24] of an $H_2$ unit in an $H_{2n}$ chain, and $\mu_4 < 0$ is proportional to a "hyperhardness." Setting to zero the derivative of Eq. (2) with respect to $\delta$ gives

$$0 = 4\mu_2\delta + 8\mu_4\delta^3 - Fl. \tag{3}$$

Under the assumption that the field $F$ is weak and $\delta$ is small, this cubic equation can be solved by iteration. The first iteration gives $\delta=(l/4\mu_2)F$, and the second gives

$$\delta = \frac{l}{4\mu_2}F - \frac{\mu_4 l^3}{32\mu_2^4}F^3. \tag{4}$$

The energy change associated with this charge transfer is found by inserting Eq. (4) into Eq. (2) and truncating at order $F^4$,

$$\Delta = -\frac{l^2}{8\mu}F^2 + \frac{\mu_4 l^4}{128\mu_2^4}F^4. \tag{5}$$

Equation (5) has $F^2$ and $F^4$ terms, like Eq. (1).

Finally consider the collection of all symmetric pairs of $H_2$ units in the $H_{2n}$ chain. Let the integer $j$ label the $H_2$ units, starting from $j=1$ at one end of the chain and ending at $j=n$ at the other end. If $n$ is even, there are $n/2$ symmetric pairs. If $n$ is odd, there is one unpaired (and uncharged) $H_2$ unit at the chain center, leaving $(n-1)/2$ symmetric pairs. The $j$th $H_2$ unit is the first unit of a symmetric pair if $j \leq J$, where $J$ is the number of symmetric pairs,

$$J = \begin{cases} n/2 & (n \text{ even}), \\ (n-1)/2 & (n \text{ odd}). \end{cases} \tag{6}$$

The distance between the center of the $j$th $H_2$ unit ($1 \leq j \leq$ J) and that of its symmetric partner (if it has one) is

$$l_j = (n + 1 - 2j)l_0, \tag{7}$$

which varies from a maximum of $l_1=(n-1)l_0$ to a minimum of $l_j=l_0$ (for $n$ even) or $2l_0$ (for $n$ odd), for $j \geq 1$.

The distribution of the transferred charge will be antisymmetric about the chain center, and the energy will depend on this distribution but not on how it was established. The change in the total energy due to the field $F$ is thus found by summing the contributions from all $H_2$ units and all symmetric pairs of $H_2$ units. With the help of Eqs. (1) and (5), we find that the $H_{2n}$ polarizability is

$$\alpha = \alpha_1 + \bar{\alpha}(n-1) + \frac{1}{4\mu_2}\sum_{j=1}^{J} l_j^2, \tag{8}$$

and the $H_{2n}$ hyperpolarizability is

$$\chi = \chi_1 + \bar{\chi}(n-1) - \frac{3}{16}\frac{\mu_4}{\mu_2^4}\sum_{j=1}^{J} l_j^4. \tag{9}$$

The charge-transfer terms in Eqs. (8) and (9) introduce a highly nonlinear dependence on chain length $l_0 n$. In the limit of large $n$, the sums over $j$ in Eqs. (8) and (9) can be replaced by integrals which become $(l_0 n)^3/(6l_0)$ and $(l_0 n)^5/(10l_0)$, respectively. In a three-dimensional solid constructed by parallel stacking of identical long chains, these terms would be suppressed by the electrostatic interactions among the transferred charges, because volume charge densities in macroscopic solids are energetically unacceptable. (For example, the energy of a sphere of radius $R$ containing a uniform charge density increases as $R^5$, much faster than the volume.) For short single linear chains, however, the electrostatic interactions among the transferred charges are almost negligible, as shown in Appendix B.

## III. RESULTS AND DISCUSSION

For $H_{2n}$ chains with $n \leq 7$, and for electric fields with $|F| \leq 0.008$ a.u., the first term in the energy change of Eq. (1) is of order millihartrees, and the second is less than or equal to about 1% of the first, as shown in Fig. 1.

The parameters of our model are presented in Table I. The polarizability $\alpha_1$ and hyperpolarizability $\chi_1$ for a single $H_2$ unit ($n=1$) were computed self-consistently by the method described in Appendix A, which refines the method of Ref. [16]. The infinite-chain parameters $\bar{\alpha}$ and $\bar{\chi}$, the chemical hardness parameter $\mu_2$, and the hyperhardness parameter $\mu_4$ were found by least-squares-error fitting of our Eqs. (8) and (9) [with the small corrections of Eqs. (B5) and (B6)] to the polarizabilities $\alpha$ and hyperpolarizabilities $\chi$ for $H_{2n}$ chains with $n \leq 7$, as calculated self-consistently in Appendix A. Note from Table I that $\mu_2$ in the Hartree-Fock (HF) approximation is about 3 times larger than it is in the local spin-density (LSD) approximation. This result is in accord with the interpretation of Ref. [16]: Self-interaction correction makes the electrons stick tighter to the $H_2$ units, making it harder to move the electron number on a unit away from the integer 2. In the limit where the $H_2$ units become far separated from one another, a kink or derivative discontinuity appears at $N=2$ in the exact energy of a chain unit as a function of the number $N$ of electrons on it, and LSD fails to produce the correct derivative discontinuity while HF more nearly produces it. In the language of Refs. [12–15], HF is more nearly "many-electron self-interaction-free" than LSD is.

For $H_4$, there is only one charge transfer $\delta$, from the first $H_2$ unit to the second and last one. Figure 2 plots our Eq. (2) for the energy change associated with this charge transfer, first for no electric field ($F=0$) and then for $F=0.008$ a.u. It is clear from Fig. 2 that an $H_2$ unit in $H_4$ is chemically harder in HF than in LSD, and as a result the field is able to transfer less charge after self-interaction correction.

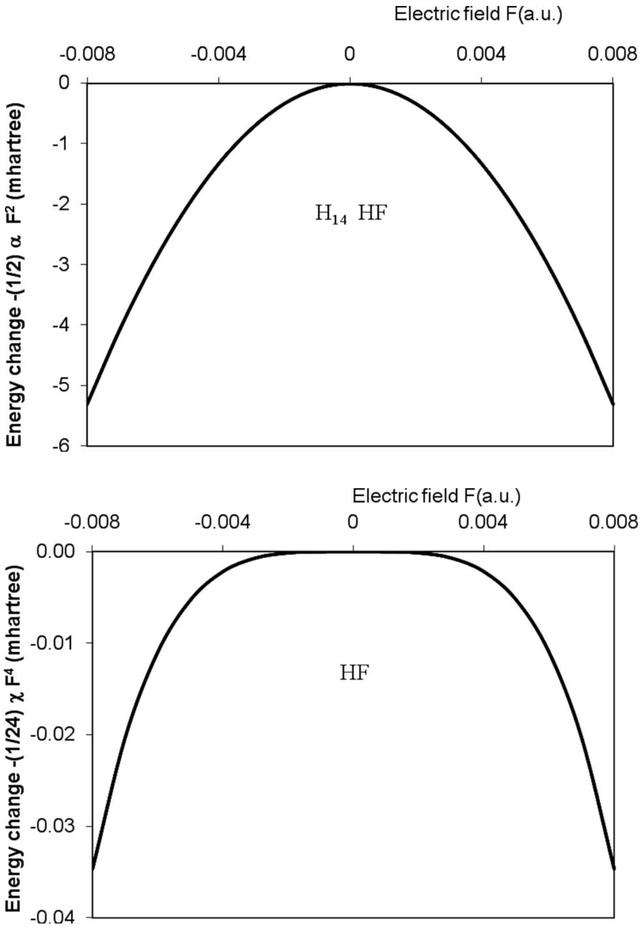

FIG. 1. Energy change of Eq. (1) vs electric field $F$ for an $H_{14}$ chain. The upper panel is the polarizability term, and the lower panel is the hyperpolarizability term. $\alpha=165.7$ a.u. and $\chi=202\,900$ a.u. from the self-consistent HF calculations of Appendix A and Ref. [16].

Equation (4) with $l=l_j$ of Eq. (7) determines the model distribution of transferred charge over the $H_2$ units labeled $j=1,2,\ldots,n$. Figure 3 shows this distribution for $H_{14}$ at the HF level. Note that the charge is antisymmetric about the chain center.

Since the main difference in the model parameters is that $\mu_2(\text{HF}) \gg \mu_2(\text{LSD})$, Eqs. (8) and (9) show that self-interaction correction will reduce $\alpha$ somewhat $(\sim\mu_2^{-1})$ and $\chi$ by much more $(\sim\mu_2^{-4})$. Figures 4 and 5 confirm this, and also show the mild nonlinearity of $\alpha$ as a function of $n$, and the stronger nonlinearity of $\chi$ as a function of $n$, which can also be understood from Eqs. (8) and (9) as discussed in Sec. II.

TABLE I. Parameters (in a.u.) of the charge-transfer model for the electrical response of $H_{2n}$ chains. $\alpha_1$ and $\chi_1$ are computed self-consistently for a single $H_2$ unit, while $\bar{\alpha}$, $\bar{\chi}$, $\mu_2$, and $\mu_4$ were fitted to such calculations for $1 \leqslant n \leqslant 7$. ($l_0=5$ bohr.)

| Parameters | LSD | HF |
|---|---|---|
| $\alpha_1$ | 12.6 | 12.4 |
| $\chi_1/10^3$ | 1.09 | 0.35 |
| $\bar{\alpha}$ | 29.3 | 21.8 |
| $\bar{\chi}/10^3$ | 87.0 | 20.4 |
| $\mu_2$ | 4.51 | 14.66 |
| $\mu_4$ | −4285.0 | −21930.0 |

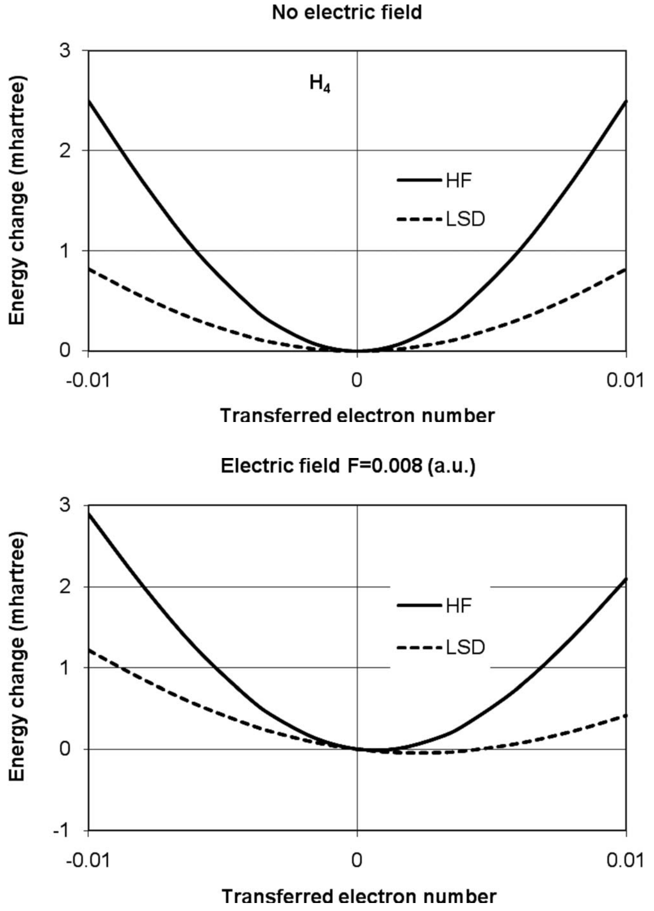

FIG. 2. Energy change Δ vs transferred electron number $\delta$ for an $H_4$ chain, using model parameters from Table I. The upper panel is without electric field, and the lower panel is for electric field $F=0.008$ a.u.

The Coulomb interaction among the transferred charges has been treated as a first-order perturbation in our model. Table II and Appendix B show that this treatment is justified for linear $H_{2n}$ chains with $n \leqslant 7$, although this interaction

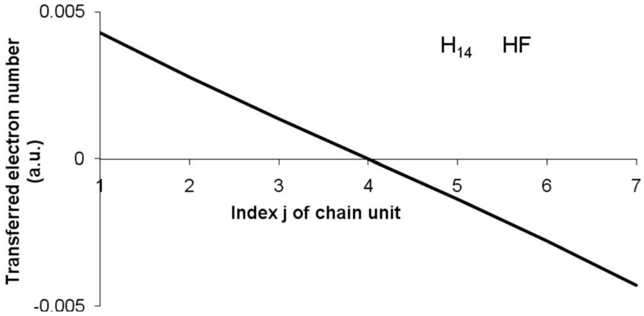

FIG. 3. Electron number $\delta$ transferred to the $j$th chain unit in $H_{14}$ vs $H_2$ unit index $j$, for $H_{14}$ in electric field $F=0.008$ a.u., using model parameters from Table I. The electric field points to the right-hand-side and drives electrons to the left-hand-side.

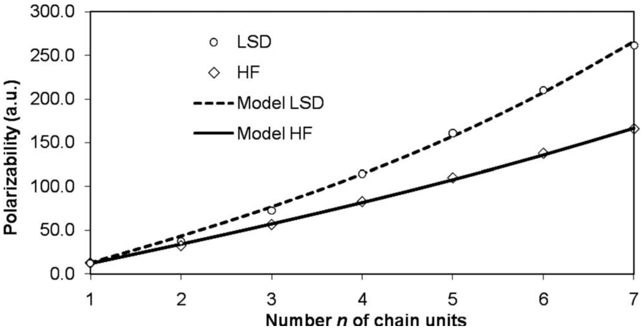

FIG. 4. Polarizability $\alpha$ vs number $n$ of chain units in $H_{2n}$. The dashed and solid curves are based on the model with parameters from Table I, fitted to self-consistent LSD and HF values of Appendix A (shown as circles and diamonds, respectively).

starts to suppress the electrical response coefficients for $n \geqslant 6$.

In summary, our model shows that the strong nonlinearity of the polarizability and hyperpolarizability of an $H_{2n}$ chain as functions of $n$ are to a considerable extent consequences of charge transfer between $H_2$ units. This transfer is not suppressed by Coulomb interaction among the transferred charges for linear chains with $n \leqslant 7$, although it may be strongly suppressed in three-dimensional solids or in longer single chains. The model also shows that local and semilocal functionals exaggerate the charge transfer because they predict too little chemical hardness for the $H_2$ units within the chain, and that self-interaction correction (as present, for example, in HF) reduces and corrects the electrical response by predicting a larger and more realistic hardness.

## IV. VALIDATION AND LIMITATIONS OF THE PHYSICAL PICTURE BEHIND THE MODEL

To validate and delimit the physical picture behind our model, we revert to self-consistent electronic structure calculations for the $H_{2n}$ chains, as in Ref. [16]. We need a population analysis to simplify the calculated charge density by representing it as a collection of point charges.

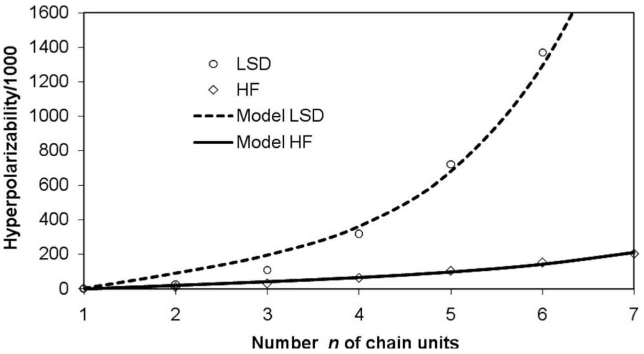

FIG. 5. Longitudinal second hyperpolarizability $\chi$ (in a.u.) vs number $n$ of chain units in $H_{2n}$. Here $\chi/10^3$ is displayed. The dashed and solid curves are based on the model with parameters from Table I, fitted to self-consistent LSD and HF values of Appendix A (shown as circles and diamonds, respectively). The off-scale $n=7$ LSD values are self-consistent 2270, model 2325.

TABLE II. Model results (in a.u.) for the longitudinal polarizability $\alpha$ and second hyperpolarizability $\chi$ of $H_{2n}$ chains, without and with the effect of the Coulomb (+C) interaction between the transferred charges, for HF.

| $n$ | $\alpha$ | $\alpha$(+C) | $\chi/10^3$ | $\chi$(+C)$/10^3$ |
|---|---|---|---|---|
| 1 | 12.4 | 12.4 | 0.35 | 0.35 |
| 2 | 34.6 | 34.6 | 20.8 | 20.8 |
| 3 | 57.7 | 57.7 | 42.0 | 42.1 |
| 4 | 82.1 | 82.1 | 66.1 | 66.1 |
| 5 | 108.1 | 108.1 | 97.1 | 97.0 |
| 6 | 136.3 | 136.3 | 141.7 | 141.3 |
| 7 | 167.1 | 166.9 | 210.0 | 208.6 |
| 10 | 278.9 | 278.3 | 721.9 | 705.1 |
| 20 | 993.6 | 983.5 | 18045.0 | 16929.0 |
| 50 | 9959.0 | 9694.0 | 1737420.0 | 1547449.0 |

The Mulliken, natural (NPA) and ChelpG (charges from electrostatic potentials using a grid) population analyses (as provided by the computer code of Ref. [25]) of the HF and LSD electron densities for $H_{14}$ show that there are net charges on the $H_2$ units even in the absence of field. Due to the large diffuse basis set necessary for polarizability and hyperpolarizability calculations, the Mulliken charges show inconsistent random behavior and cannot be used for our purposes. NPA charges behave better than Mulliken charges, but they show nonsymmetric (unphysical) oscillations in the middle of the chain. The HF and LSD ChelpG charges are shown in Table III. The ChelpG method gives the central $H_2$ unit of the $H_{14}$ chain a very small positive charge

TABLE III. ChelpG atomic charges (in a.u.) for the atoms of the $H_2$ units in an $H_{14}$ chain, in the absence of the electric field and in the presence of an $F=0.008$ a.u. electric field along the chain. The LSD and HF calculations use the 6-311++G($d$,$p$) basis set.

| | | LSD | | HF | |
|---|---|---|---|---|---|
| Unit ($j$) | Atom ($i$) | $F=0$ | $F=0.008$ | $F=0$ | $F=0.008$ |
| 1 | 1 | 0.051 | −0.041 | 0.052 | −0.018 |
| 1 | 2 | −0.080 | −0.021 | −0.086 | −0.025 |
| 2 | 1 | 0.060 | −0.017 | 0.068 | −0.004 |
| 2 | 2 | −0.043 | 0.015 | −0.048 | 0.020 |
| 3 | 1 | 0.022 | −0.046 | 0.025 | −0.047 |
| 3 | 2 | −0.013 | 0.047 | −0.014 | 0.056 |
| 4 | 1 | 0.003 | −0.060 | 0.004 | −0.068 |
| 4 | 2 | 0.003 | 0.066 | 0.004 | 0.075 |
| 5 | 1 | −0.013 | −0.073 | −0.014 | −0.085 |
| 5 | 2 | 0.022 | 0.090 | 0.025 | 0.097 |
| 6 | 1 | −0.043 | −0.099 | −0.048 | −0.115 |
| 6 | 2 | 0.060 | 0.133 | 0.068 | 0.139 |
| 7 | 1 | −0.080 | −0.131 | −0.086 | −0.144 |
| 7 | 2 | 0.051 | 0.135 | 0.052 | 0.119 |

TABLE IV. ChelpG charges transferred by the longitudinal electric field $F=0.008$ a.u. to each of the $H_2$ units in a linear $H_{14}$ chain. These results are based upon Table III, and are qualitatively similar to the model prediction of Fig. 3. The transferred charge is defined as $qct_j=q_{j,1}(F=0.008)+q_{j,2}(F=0.008)-q_{j,1}(F=0)-q_{j,2}(F=0)$, where $q_{j,i}$ is the ChelpG charge of the $i$th atom of the $j$th $H_2$ unit in Table III.

| Unit ($j$) | LSD | HF |
|---|---|---|
| 1 | −0.033 | −0.009 |
| 2 | −0.018 | −0.004 |
| 3 | −0.008 | −0.001 |
| 4 | 0.000 | 0.000 |
| 5 | 0.008 | 0.001 |
| 6 | 0.018 | 0.004 |
| 7 | 0.033 | 0.009 |

(0.007 a.u.) and no dipole; the polarity of the $H_2$ units increases towards the chain ends (cf. Table III). The ChelpG charges provide a reasonable physical picture, so we have used ChelpG charges for comparison with our model. In the ChelpG scheme [26], the point charges are chosen to reproduce the electrostatic potential at a number of points around the outside of the molecule. (For $H_{14}$, about 14 000 points were fitted.)

Applying an $F=0.008$ a.u. electric field along the $H_{2n}$ chain changes the atomic charges and the charges of the $H_2$ units (cf. Tables III and IV). The field-driven charge transfer between $H_2$ units (Table IV) is qualitatively like that in the model (Fig. 3), when we recall that transferred charge and transferred electron number are equal and opposite in atomic units. The dipole moments induced by the electric field in the absence of charge transfer are shown in Table V and are approximately $[\alpha_1/n+\bar{\alpha}(1-1/n)]F+[\chi_1/n+\bar{\chi}(1-1/n)]F^3/6$ per chain unit, as in the model. In detail, the HF and LSD induced dipole moments behave differently: In HF the largest dipole moment is induced in the middle of the chain, while in LSD the largest dipole moments are induced at the chain ends (cf. Table V).

TABLE V. The dipole moment (in a.u.) induced on each $H_2$ unit of a linear $H_{14}$ chain by the longitudinal electric field $F=0.008$ a.u., calculated from the ChelpG atomic charges of Table III. The charge transferred to an $H_2$ unit by the field (Table IV) has been taken out, leaving equal and opposite induced charges ($\pm qdip_j$) on each H atom in that unit at a separation of $a=2$ bohr, with dipole moment $qdip_j a$. In the notation of the caption of Table IV, $qdip_j=q_{j,2}\ (F=0.008)-q_{j,2}\ (F=0)-qct_j/2$. For comparison, our model predicts equal induced dipole moments $[\alpha_1/n+\bar{\alpha}(1-1/n)]F+[\chi_1/n+\bar{\chi}(1-1/n)]F^3/6$ (0.222 in LSD, 0.165 in HF) on all units.

| Unit ($j$) | LSD | HF |
|---|---|---|
| 1 | 0.151 | 0.131 |
| 2 | 0.135 | 0.140 |
| 3 | 0.127 | 0.143 |
| 4 | 0.126 | 0.144 |
| 5 | 0.128 | 0.143 |
| 6 | 0.130 | 0.139 |
| 7 | 0.135 | 0.125 |

TABLE VI. Increase in the electronic spatial extent, $\Delta\langle r^2\rangle = \langle r^2(F=0.008)\rangle - \langle r^2(F=0)\rangle$, and the dipole and octapole moments induced along the chain by electric field $F=0.008$ a.u. in the $H_{14}$ chain. All results are in a.u. The HF and LSD calculations use the 6-311+G($d,p$) basis set.

| Property | LSD | HF |
|---|---|---|
| $\Delta\langle r^2\rangle$ | 0.5747 | 0.2537 |
| Dipole | 2.395 | 1.343 |
| Octapole | 584.9 | 362.6 |

The electric field also breaks the symmetry, increases the electronic spatial extent of the molecule, and induces large dipole and octapole moments (cf. Table VI). The results in Tables III, IV, and VI show that the LSD error manifests as a soft electron density that is deformed too strongly by the external field. The HF electron density is considerably stiffer. Thus it gives more realistic polarizabilities and hyperpolarizabilities, as does the Perdew-Zunger [10] self-interaction correction (PZ-SIC) in our previous study [16]. In that study we have suggested that PZ-SIC performs like Hartree-Fock theory for the electrical response. This is because each $H_2$ unit of an $H_{2n}$ chain is a partly isolated open system in which the average electron number is not integer. Over such a system, the exchange-hole density around an electron integrates to the same number in PZ-SIC as in Hartree-Fock theory. Thus the exchange energy (exact in Hartree-Fock theory) of this open system is described well by PZ-SIC, leading to approximate many-electron self-interaction freedom [16,27]. However, the exchange energy of the semilocal density functionals is not correct as their exchange-hole density around an electron integrates to an incorrect number. In this study we do not repeat our earlier PZ-SIC numbers; the interested reader should refer to our PZ-SIC results in Ref. [16]. We also note that the software [25] used for the present study does not support SIC.

Our model qualitatively describes the charge transfer among $H_2$ chain units driven by the electric field, and its consequences. We omit several effects which, if included, could lead to a more accurate but overfitted description: (1) There are charge transfers even at zero field, driven by standing waves from the chain ends. (2) The hardness and hyperhardness of a chain unit could be greater for a unit near the chain end than for one in an infinite chain. (3) The non-charge-transfer contributions to the response coefficients could show a nonlinear length dependence for chains of short length.

## ACKNOWLEDGMENT

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## APPENDIX A: PROCEDURE TO OBTAIN PRECISE SECOND HYPERPOLARIZABILITY FROM THE CALCULATED ENERGIES

The approach in our previous paper [16] was to make a least squares fit of Eq. (1) to calculated energies for evenly spaced fields $F$ in the range $0 < F < F_{\max}$. In this approach when $F_{\max}$ is too small, the second hyperpolarizability is too small to resolve. When $F_{\max}$ is too large, the contributions of higher hyperpolarizabilities cannot be ignored. In that work, we choose $F_{\max}=0.007$ a.u. For the longer chains treated with semilocal functionals, this $F_{\max}$ may be too large for optimum accuracy. In this appendix we shall investigate the effect of this choice of $F_{\max}$.

To avoid the contribution of the first-order hyperpolarizability and enhance the numerical accuracy, we used the inversion symmetry of the hydrogen chains to construct and fit to an even function for the energy versus electric field. This way the odd coefficients disappear for the energy polynomial. A fourth-order polynomial was used in the fitting procedure to the energy [cf. Eq. (1)]. This procedure gave accurate and stable polarizability values. However, the second hyperpolarizability shows extreme sensitivity to any change of (or numerical error in) the calculated energy, leading to an uncertainty of about ±20% in the SIC, LSD, and Perdew-Burke-Ernzerhof (PBE) values. In order to decrease this uncertainty we have developed alternative and more precise ways to calculate the second hyperpolarizability, as presented below.

The longitudinal polarizability $\alpha$ and second hyperpolarizability $\chi$ of an $H_{2n}$ chain can be calculated by applying twice Eq. (1) for two different fields $F_i$ and $F_j$ and solving the two linear equations for $\alpha$ and $\chi$,

$$\alpha = \frac{\dfrac{2(E_{n,i}-E_{n,1})F_j^4}{F_i^4} - 2(E_{n,j}-E_{n,1})}{F_j^2 - \dfrac{F_j^4}{F_i^2}}, \tag{A1}$$

$$\chi/1000 = \frac{0.024\left(\dfrac{(E_{n,i}-E_{n,1})F_j^2}{F_i^2} - E_{n,j} + E_{n,1}\right)}{F_j^4 - F_j^2F_i^2}, \tag{A2}$$

where $E_{n,1}$ is the total energy of the $H_{2n}$ chain without field, while $E_{n,i}$ and $E_{n,j}$ are the total energies in the presence of fields $F_i$ and $F_j$, respectively. The correctness of the $\alpha$ and $\chi$ obtained this way can be checked by applying multiple fields. Our analysis shows that these simple formulas give reasonably consistent results for HF and Møller-Plesset (MP3) energies in the range of $F=0.005-0.008$ a.u. However, for LSD or PBE Eq. (A2) might give imprecise, field-dependent values in the range $F=0.001-0.008$ a.u. For small $n$ a small $F$ gives random second hyperpolarizability values due to numerical errors, while for large $n$ a large $F$ gives a serious overestimation of $\chi$ because the higher hyperpolarizabilities cannot be ignored. Equation (A1) performs somewhat better, but not completely satisfactorily. To illustrate the problems, we present some details. For the $H_{14}$ chain with LSD, the choice $F_i=0.007$ and $F_j=0.008$ a.u. gives $\alpha=257.02$ a.u. and $\chi/1000=3729.8$ a.u. This result can be compared to the accurate polarizability calculated analytically by GAUSSIAN 03 using the polar keyword, $\alpha=261.73$ a.u. Using the choice $F_{\mathrm{i}}=0.002$ and $F_j=0.003$ a.u. gives $\alpha=261.62$ a.u. and $\chi/1000=2246.4$ a.u. This shows that for LSD or PBE inclusion of large field energies into the fitting can seriously deteriorate the results for longer chains ($n>3$), so relatively small fields must be applied. The range of the applied electric fields can be estimated by assuming that an ideal maximum field $F_{\max}$ makes the $\chi$ term of Eq. (1) a fixed small fraction $C$ of the $\alpha$ term. Then

$$F_{\max} = \sqrt{12\frac{\alpha}{\chi}C}. \tag{A3}$$

Trial and error suggests $C \approx 0.01$. This formula gives for LSD or PBE $F_{\max}=0.013$, 0.009, 0.007, 0.005, 0.004, 0.0036, and 0.003 a.u. for $H_{2n}$ chains of $n=2$, 3, 4, 5, 6, 7, and 8, respectively. Figure 6 shows the dependence of $F_{\max}$ from Eq. (A3) on $n$.

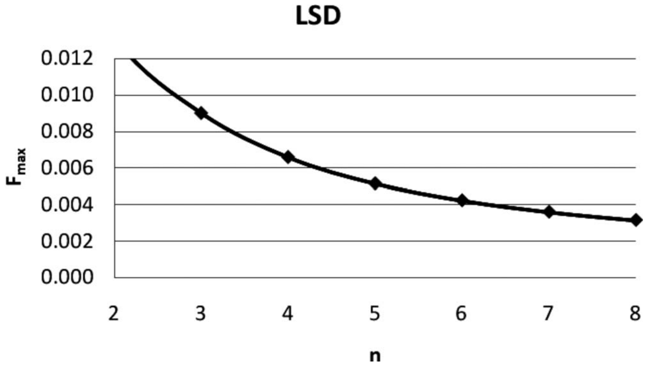

FIG. 6. Dependence of $F_{\max}$ on $n$ for the LSD second hyperpolarizability $\chi$, for $H_{2n}$ chains, from Eq. (A3).

Second hyperpolarizabilities can be obtained alternatively by using Eq. (1) and a precise (polar keyword) estimation for $\alpha$. In this way, we obtained a series of $\chi$'s for various field strengths. We observed that, for larger $F$ values than our $F_{\max}$, the value of $\chi$ starts to increase (due to higher order terms). In our previous paper we used the large field values in the fitting procedure, and that biased considerably the LSD and PBE values that were overestimated by at most 30%. In this paper we use $\chi$ values that were obtained for

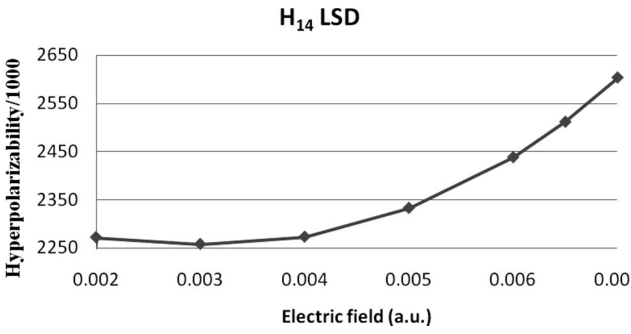

FIG. 7. LSDA second hyperpolarizability $\chi$ (a.u.): Dependence on the electric field strength for the $H_{14}$ chain.

TABLE VII. Longitudinal polarizabilities $\alpha$ (in atomic units) of linear $H_{2n}$ chains, calculated accurately and self-consistently by the method of Appendix A.

| $n$ | LSD | PBE | HF | MP3 |
|---|---|---|---|---|
| 1 | 12.6 | 12.1 | 12.4 | 11.3 |
| 2 | 37.5 | 36.0 | 32.2 | 29.9 |
| 3 | 72.7 | 69.0 | 56.4 | 52.7 |
| 4 | 114.6 | 108.0 | 82.6 | 77.5 |
| 5 | 161.2 | 150.8 | 109.9 | 103.3 |
| 6 | 210.5 | 195.9 | 137.6 | 129.6 |
| 7 | 261.6 | 242.4 | 165.7 | 156.2 |

TABLE VIII. Longitudinal second hyperpolaribilities $\chi$ (in atomic units) of linear $H_{2n}$ chains, calculated accurately and self-consistently by the method of Appendix A. $\chi/10^3$ is displayed.

| $n$ | LSD | PBE | HF | MP3 |
|---|---|---|---|---|
| 1 | 1.09 | 0.81 | 0.35 | 0.58 |
| 2 | 23.6 | 21.4 | 9.8 | 10.5 |
| 3 | 106 | 95.7 | 30.2 | 34.0 |
| 4 | 315 | 281 | 62.2 | 73.2 |
| 5 | 721 | 624 | 103.7 | 127.5 |
| 6 | 1370 | 1130 | 152.0 | 191.5 |
| 7 | 2270 | 1820 | 202.9 | 259.8 |

field strengths about $F_{\max}$. This procedure gives for $H_{14}$ LSD $\chi \cong 2270$ a.u., somewhat (22%) smaller than our previous estimate of 2900 a.u. Our new estimation has a possible 2% error. Figure 7 shows how the LSD second hyperpolarizability $\chi$ depends on the applied field strength for the $H_{14}$ linear chain.

Our accurate numerical results are shown in Tables VII and VIII. We note that the HF method with a triple-zeta polarized basis set gives a reasonable estimate of the polarizability, since the effect of electron correlation is small. The hyperpolarizabilities are more sensitive to electron correlation and to basis set, requiring diffuse functions for reliable calculated values. The HF method slightly overestimates the polarizabilities and underestimates the longitudinal hyperpolarizabilities, in comparison with third-order many-body perturbation theory (MP3). These observations are in agreement with those of Ref. [28].

## APPENDIX B: PERTURBATIVE TREATMENT OF THE COULOMB INTERACTION AMONG TRANSFERRED CHARGES

The contribution to the energy from Coulomb interaction among transferred charges is the sum over all distinct pairs (including unsymmetric pairs)

$$\sum_{j=1}^{n} \sum_{j'=j+1}^{n} \frac{\delta_j \delta_{j'}}{(j'-j) l_0}. \tag{B1}$$

$\delta_j$ is given by Eqs. (4) and (7),

$$\delta_j = a_j F + b_j F^3, \tag{B2}$$

$$a_j = \frac{1}{4\mu_2} l_j, \tag{B3}$$

$$b_j = -\frac{\mu_4}{32\mu_2^{\,4}} l_j^{\,3}. \tag{B4}$$

Using Eq. (1) we find that the polarizability changes by

$$-2\sum_{j=1}^{n} \sum_{j'=j+1}^{n} \frac{a_j a_{j'}}{(j'-j) l_0}, \tag{B5}$$

and the hyperpolarizability by

$$-24\sum_{j=1}^{n} \sum_{j'=j+1}^{n} \frac{a_j b_{j'} + a_{j'} b_j}{(j'-j) l_0}. \tag{B6}$$

The relative contributions from (B5) and (B6) are very small (Table II), justifying the first-order perturbation treatment applied here. A nonperturbative treatment would involve solving linear equations for the $a_j$ and $b_j$.

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